Enhanced Introductory College Chemistry

ENHANCED INTRODUCTORY COLLEGE CHEMISTRY

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Original OER Sources

This OER, *Enhanced Introductory College Chemistry*, is a collection of resources adapted to meet the needs of students in introductory chemistry courses. In most sections of this OER, updates have been made to the existing content to improve usability and accessibility, incorporate interactive elements and improve the overall student experience. Except where otherwise noted, images and diagrams are derived from the source attributed at end of each page. This OER adaptation reuses content from the following key resources:

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Please submit feedback to OER[at]georgiancollege.ca

Disclaimer

We have done our best to acknowledge all participants involved in this project. In the event, we have made an error please reach out to the project manager to have this corrected.

LAND ACKNOWLEDGEMENTS

Georgian College

Georgian College acknowledges that all campuses are situated on the traditional land of the Anishnaabeg people. The Anishnaabeg include the Odawa, Ojibwe and Pottawatomi nations, collectively known as the Three Fires Confederacy. Georgian College is dedicated to honouring Indigenous history and culture and committed to moving forward in the spirit of reconciliation and respect with all First Nations, Métis and Inuit people.

Loyalist College

Loyalist College is located on the territory of the Huron-Wendat, the Anishnaabeg, and the Haudenosaunee people. We acknowledge our shared obligation to respect, honour, and sustain these lands and the natural resources contained within.

Conestoga College

At Conestoga College, we would like to acknowledge that in Kitchener, Waterloo, Cambridge and Brantford we are located on the Haldimand Tract, land promised to the Haudenosaunee people of Six Nations, which includes six miles on either side of the Grand River. This is the traditional territory of the Anishnawbe, Haudenosaunee, and Neutral peoples. To recognize the land is an expression of gratitude and appreciation to those whose territory we reside on, and a way of honouring the Indigenous people who have been living and working on the land for thousands of years.

COMMITMENT TO EQUITY, DIVERSITY, INCLUSION AND INDIGENIZATION IN CHEMISTRY

Equity, Diversity, and Inclusion in Chemistry

Our colleges (Equity, diversity, inclusion & belonging – Georgian College [New Tab] recognize the need to support and encourage equity, diversity, inclusion and belonging (EDIB) in our teaching practices. When discussing equity, diversity and inclusion in the context of a chemistry classroom, the nature of the traditional science classroom and way of learning need to be questioned. In compiling this resource, the contributors have made conscious efforts to include examples of diversity of representation with chemistry scholars.

But examples of diversity of scholars are only the start of incorporating EDIB chemistry teaching. So much more comes from how the conversations about the development and progression of chemistry are led and respected in the classroom environment. It starts with the building of an inclusive community through respect and understanding of everyone's contribution to the classroom. It continues through the development of a metanarrative to the science content. And it continues further through the acknowledgement that objectivity is not singular but multifaceted. Below are suggestions of discussion topics that faculty and students can use to encourage the inclusion of EDIB.

- What questions were asked and who was allowed to ask those questions as the science of chemistry developed?
- Whose agenda and research received funding and support to "discover" these scientific concepts?
- Who was hired to teach the next generation and lead the conversations about chemistry?
- Whose interests and pursuits are followed?
- In pharmaceutical industry (for example), who were the subjects that were used for testing?
- In industrial chemical industry (for example), who had to become ill or die to know that a chemical was toxic?
- What experiences did individuals have in their chemistry careers (personalize this whenever possible)?
- Who is working in the background of the famous discoveries?
- How is the history of erasure and the value of representation included in chemistry?
- What might this area of study or concept have looked like if a female/visible minority/LGBTQ2+ person have discovered it?

To further support EDIB within chemistry and science faculties, consider:

- Setting up a committee of peers to review curriculum, hiring and other components of program areas
- Creating a culture of support for future scholars and researchers
- Offering opportunities to complete critical inquiry and equity analysis of curriculum
- Joining existing organizations working to promote EDI initiatives in science and chemistry

Several chemistry departments at Ontario and Canadian institutions are publicly stating their commitment to EDIB. Read statements from University of Toronto [New Tab], University of Waterloo [New Tab] and University of British Columbia [New Tab]. The Chemical Institute of Canada (CIC) [New Tab] promotes EDI initiatives and there are local groups across the country representing the Canadians Working for Inclusivity in Chemical Sciences, Engineering and Technology (CWIC) Network [New Tab]. Georgian College is a facilitating participant with the Inclusive STEM Teaching Project [New Tab] working to support educators in their EDIB development.

In addition to the scientists highlighted in this resource, all scientists represent diverse cultures and experiences. Here are some suggested resources to expand the EDIB conversation:

- American Chemistry Society Reactions (Twitter: @ACSReactions) has a commemoration tweet of Juneteenth2022 highlighting Black chemists and their impact on our lives. Reactions on Twitter: "To commemorate #juneteenth2022 we're looking at handful of Black chemists and the impact they've made on our lives. Meet Alice Ball. She developed the "Ball Method," which was the most effective treatment for leprosy during the early 20th century. https://t.co/d7dnkmJ4ui" / Twitter [New Tab]
- Compound Interest (curated by Andy Brunning) has a Women in Chemistry category of infographics that highlights 100s of women throughout history and today who excel in the field of chemistry. Women in Chemistry – Compound Interest (compoundchem.com) [New Tab]
- "My STEM Stories" presented by CWIC is a YouTube channel with video highlights of some amazing current STEM researchers and scientists. "My STEM Stories" presented by CWIC – YouTube [New Tab]
- Journal of Chemical Education published an entire special issue dedicated to Diversity, Equity, Inclusion and Respect in Chemistry Education Research and Practice. Journal of Chemical Education | Vol 99, No 1 (acs.org) [New Tab]
- C&EN (Chemical and Engineering News) published Out and Proud Celebrating LGBTQ+ chemists (Out and proud (acs.org) [New Tab]) and a Movers and Shakers article highlighting LGBTQ+ chemists past and present. LGBTQ+ chemists you should know about (acs.org) [New Tab]
- Royal Society of Chemistry offers an LGBT+ toolkit to support inclusivity. LGBT+ toolkit (rsc.org) [New Tab]

Indigenization in Chemistry

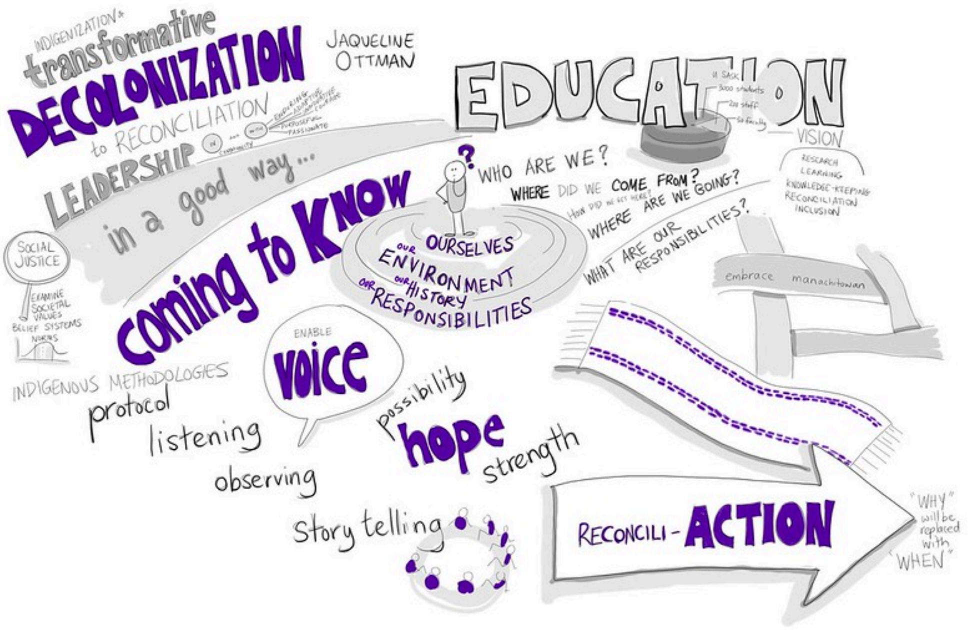
In 2015, the Truth and Reconciliation Commission of Canada (TRC), led by Honourable Justice Murray Sinclair, released Honouring the Truth, Reconciling for the Future: Summary of the Final Report of the Truth and Reconciliation Commission of Canada [New Tab] [PDF]. Their extensive consultative research process resulted in 94 Calls to Action (CTA) in order to begin dismantling the systemic racism devastating Indigenous Peoples in Canada. The CTA are outlined in What Are the Truth & Reconciliation Commission's 94 Calls to Action & How Are We Working Toward Achieving Them Today? (reconciliationeducation.ca) [New Tab] When considering how to incorporate actions towards reconciliation in the chemistry classroom, we need to start by educating ourselves on the true history of Canada and our personal acknowledgement to the land on which we live.

"Education got us into this mess and education will get us out of it." (Renkas, 2021)

"Education is the key to walking on this journey of reconciliation. Teachers in particular have a sacred responsibility to ensure that all their children, regardless of their heritage, are able to think about four key questions throughout their education:

"Where do I come from?", "Where am I going?", "Why am I here?", and most importantly, "Who am I?"" (Ore, 2021) (Waters et al., 2022)

~ Honourable Justice Murray Sinclair (chair of the Truth and Reconciliation Commission)



The journey from decolonization to reconcili-ACTION through transformation of coming to know with voice and hope and education. (credit: work by Giulia Forsythe, CC BY 2.0)

Our colleges (Indigenization – Georgian College [New Tab]) continue to strive to meet the education related CTAs. One step in that journey is the 2022 release of the Indigenization Strategy [New Tab]. When discussing Indigenous ways of knowing (IWK) in the context of a chemistry classroom, the nature of the traditional science classroom and way of learning need to be questioned. In compiling this resource, the contributors have made conscious efforts to include examples of Indigenous uses of chemistry.

But examples of Indigenous uses of chemistry are only the start of incorporating Indigenous chemistry teaching. So much more comes from how the classroom environment and processes of learning Indigenous ways are represented and respected. It starts with the building of an inclusive community through respect and understanding of everyone's contribution to the classroom. It continues through the development of a metanarrative to the science content.

Indigenous ways of knowing (IWK) are based on principles of Respect, Relevance, Reciprocity, Responsibility, Relationality, and Care. These are reflected in the Anishnaabe's Seven Grandfather Teachings of (Manitowabi):

- Love: Love is finding peace and joy in our connection to all of Creation
- Respect: Respect is to understand that all life is sacred and part of Creation
- Bravery: Bravery is to listen to your heart and courage to do what is right
- Honesty: Honesty is to be straightforward in a kind and caring way
- Humility: Humility is being thankful and grateful knowing we belong and each has something to give
- Wisdom: Wisdom is to embrace knowledge and share our life teachings

- Truth: Truth is knowing who we are and living the Grandfather Teachings

The Indigenous Medicine Wheel. (credit: work by Littlejohn657, CC BY 4.0)

The Medicine Wheel (circle of knowledge or circle of awareness) encourages us to consider the whole person in all our actions. The circle represents the integrated connections of all aspects of oneself including the connection with the Earth and natural world. (Joseph, 2023) The yellow quadrant represents the East and the Spiritual connection to the natural world. The red quadrant represents the South and the Emotional connection to the natural world. The black quadrant represents the West and the Physical connection to the natural world. And the white quadrant represents the North and the Mental connection to the natural world. (Bell, 2022) (Zimak, 2020)

The guiding principle of Two-Eyed Seeing or Etuaptmumk (Mi'kmaw) combines the learning seen from one eye with the strengths of Indigenous knowledges and ways of knowing, and from the other eye with the strengths of Western knowledges and ways of knowing. The strengths of both eyes combine together for the benefit of all. (Institute for Integrative Science & Health, n.d.)

We have attempted to start the process of reconciliation by including Indigenous examples in this textbook. We acknowledge that significantly more work is needed to truly decolonize science education. To further support Indigenization within chemistry, science faculties and classrooms, faculty should consider:

- Inviting Indigenous elders or representatives to share their knowledge of the land and its offerings
- Having class/lab activities outside linking learning to the natural environment
- Reading UBC Science Skylight (The Science Centre for Learning and Teaching) How do I get started? Creating safer learning environments for Indigenous students in STEM at UBC [New Tab][PDF]
- Exploring How do you talk about Indigenous issues in the classroom? [New Tab] from UBC
- Reading the 94 Calls to Action and commit to making steps forward in the process of reconciliation
- Reading the Final Report from the National Inquiry into the Missing and Murdered Indigenous Women and Girls (MMIWG) [New Tab] and their Calls to Justice
- Learning more about Indigenous history and current actions in Canada. A good starting place is Skoden – Teaching, Talking and Sharing About and for Reconciliation OER book: Skoden – Simple Book Publishing (pressbooks.pub) [New Tab]
- Learning more about Indigenous chemists and chemistry in Indigenous communities:
  - University of Waterloo CHEM 13 News Magazine (Fall 2022 Special Edition entitled Chemistry and Inuit Life and Culture [New Tab]
  - Dawn Pratt [New Tab] and askenootow STEM Enterprise Inc. [New Tab]
  - Vincent Ziffle at First Nations University of Canada [New Tab]
  - Cecelia Brooks [New Tab]and Wabanaki Tree Spirit Tours & Events [New Tab]
- Listening to young Indigenous representatives discuss their careers in Fireside Chats from Future

Pathways [New Tab]

Here are some suggested resources to further explore Indigenous history, knowledge and reconciliation and connections to chemistry:

- Indigenization at Georgian [New Tab] library collection of Indigenous resources
- Indigenous Education Chemistry resources [New Tab]
- Knowing Home: Braiding Indigenous Science with Western Science, Book 1 [New Tab]
- National Centre for Truth and Reconciliation [New Tab]
- Crown-Indigenous Relations and Northern Affairs Canada [New Tab]

Attribution & References

References

Bell, D. N. (2022, March 30). *Teaching by the medicine wheel: Education Canada Magazine*. EdCan Network.

Institute for Integrative Science & Health. (n.d.). *Guiding principles (Two Eyed Seeing)*.

Joseph, B. (2023, January 12). *What is an indigenous medicine wheel?* Indigenous Corporate Training Inc.

Manitowabi, S. (2018). The Seven grandfather teachings. *Historical and Contemporary Realities: Movement Towards Reconciliation*. eCampus Ontario Open Library. Retrieved February 6, 2023.

Ore, J. (2021, September 25). *National Day for Truth and Reconciliation is 1 step on a long journey, says Murray Sinclair*. CBC News.

Renkas, A. L. (2021, July 7). *Letter: When you know better, do better*. SaskToday.ca.

Waters, L. B., Pitawanakwat, R., Dachyshyn, D., Venis, A., Catenazzo, G., Go, N., LTD, B. I. T. N., Petahtegoose, S., Redsky, E., Wabie, J.-L., Greenfield, E., & College, S. (2022, February 25). Chapter 1: Towards Truth and Reconciliation – Medicine wheel questions and activities. *Skoden*. eCampus Ontario Open Library. Retrieved February 6, 2023.

Zimak, H. (2020, June 25). *An Ontario firekeeper explains the four directions of the medicine wheel*. CBC News.

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CHAPTER 1. WELCOME TO CHEMISTRY!

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The origins of chemistry
- The scientific method
- Matter and its classifications

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Understanding of driving scientific principles – Laws, theories and hypotheses

Your alarm goes off and, after hitting "snooze" once or twice, you pry yourself out of bed. You make a cup of coffee to help you get going, and then you shower, get dressed, eat breakfast, and check your phone for messages. On your way to school, you stop to fill your car's gas tank, almost making you late for the first day of chemistry class. As you find a seat in the classroom, you read the question projected on the screen: "Welcome to class! Why should we study chemistry?"

Do you have an answer? You may be studying chemistry because it fulfills an academic requirement, but if you consider your daily activities, you might find chemistry interesting for other reasons. Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use—like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car—all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this course, you will learn many of the essential principles underlying the chemistry of modern-day life.

Indigenous Perspective: Dawn Pratt, MSc.

Figure 1a shows a Tipi at the Toronto Zoo. (credit: Photo by Samantha Sullivan Sauer, CC BY 4.0)

"To me, [Indigenizing STEM] means bringing in land-based education, bringing in the culture, bringing in the language, bringing in the Elders and the Knowledge Keepers," — Dawn Pratt.

Belonging to the Muscowpetung Saulteaux Nation, Dawn Pratt is a chemist turned educator who is on a mission to Indigenize STEM. Her venture develops a curriculum to blend Indigenous knowledge and STEM lessons. Read more about this mission in *c&en: Chemical & Engineering News* [New Tab].

Source: (Harwitz, 2021)

Attributions & References

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References

Harwitz, E. (2021, October 9). Dawn Pratt is on a mission to increase Indigenous representation in STEM, one fun science class at a time. *c&en: Chemical & Engineering News*. *99*(7). https://cen.acs.org/education/science-communication/Dawn-Pratt-mission-increase-Indigenous/99/i37

1.1 CHEMISTRY IN CONTEXT

Learning Objectives

By the end of this section, you will be able to:

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavours involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well—clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans began to practice chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. Subsequently, they began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants. Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were combined to form alloys—for example, copper and tin were mixed together to make bronze—and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation.

Attempts to understand the behaviour of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations were spread from

Egypt, China, and the eastern Mediterranean by alchemists, who endeavoured to transform "base metals" such as lead into "noble metals" like gold, and to create elixirs to cure disease and extend life (Figure 1.1.a).

Figure 1.1a This portrayal shows an alchemist's workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Alchemist's workshop by Lazarus Ercker provided by the Science History Institute, PD)

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behaviour of matter. This effort has been so successful that many people do not realize either the central position of chemistry among the sciences or the importance and universality of chemistry in daily life.

Chemistry: The Central Science

Chemistry is sometimes referred to as "the central science" due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields (Figure 1.1b). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive.

Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world's population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.

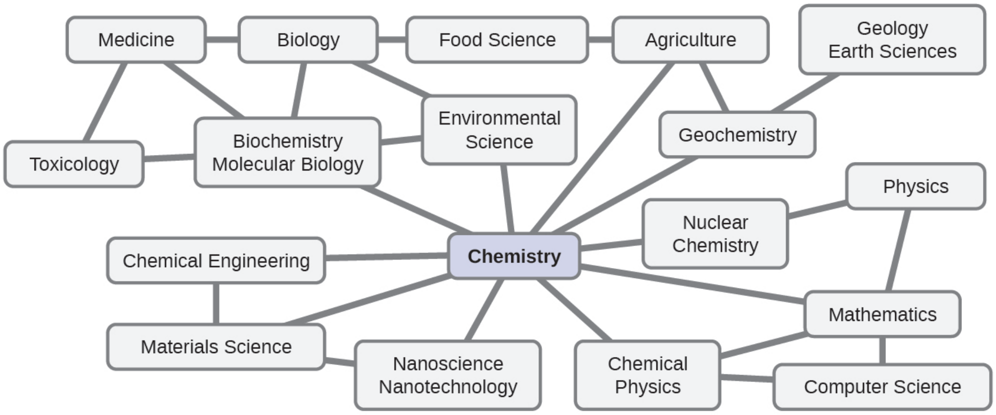

Figure 1.1b Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields. (credit: Chemistry (OpenStax), CC BY 4.0).

What are some changes in matter that are essential to daily life? Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this course, you will discover many different examples of changes in the composition and structure of matter, how to classify these changes and how they occurred, their causes, the changes in energy that accompany them, and the principles and laws involved. As you learn about these things, you will be learning **chemistry**, the study of the composition, properties, and interactions of matter. The practice of chemistry is not limited to chemistry books or laboratories: It happens whenever someone is involved in changes in matter or in conditions that may lead to such changes.

The Scientific Method

Chemistry is a science based on observation and experimentation. Doing chemistry involves attempting to answer questions and explain observations in terms of the laws and theories of chemistry, using procedures that are accepted by the scientific community. There is no single route to answering a question or explaining an observation, but there is an aspect common to every approach: Each uses knowledge based on experiments that can be reproduced to verify the results. Some routes involve a **hypothesis**, a tentative explanation of observations that acts as a guide for gathering and checking information. We test a hypothesis by experimentation, calculation, and/or comparison with the experiments of others and then refine it as needed.

Some hypotheses are attempts to explain the behaviour that is summarized in laws. The **laws** of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of explaining a large body of experimental data, it can reach the status of a theory. Scientific **theories** are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory explanations, but they can be modified if new data become available. The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the **scientific method** (Figure 1.1c).

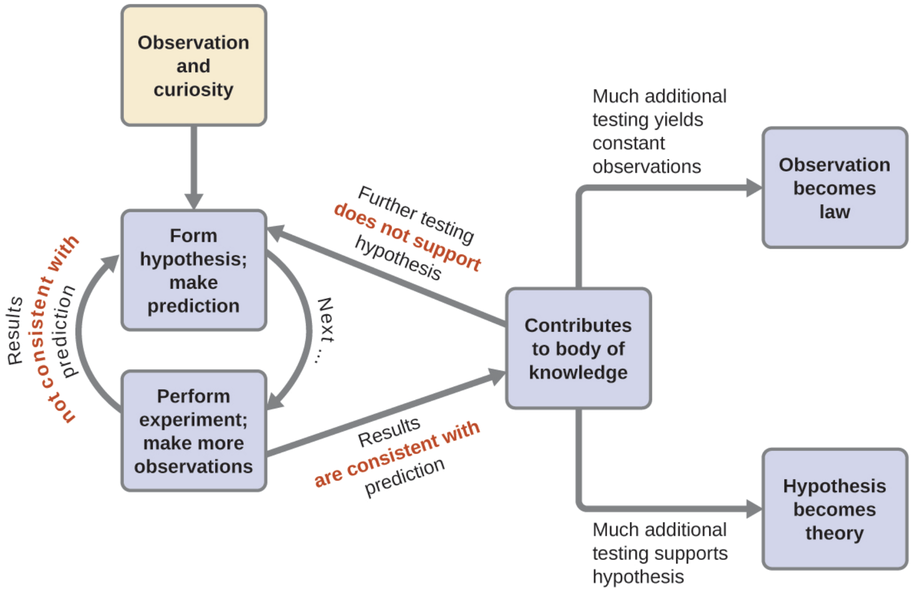

Figure 1.1c The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings (credit: Chemistry (OpenStax), CC BY 4.0).

The Domains of Chemistry

Chemists study and describe the behaviour of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of considering and describing chemical behaviour.

Macro is a Greek word that means “large.” The **macroscopic domain** is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain includes every day and laboratory chemistry, where we observe and measure physical and chemical properties, or changes such as density, solubility, and flammability.

The **microscopic domain** of chemistry is almost always visited in the imagination. *Micro* also comes from Greek and means “small.” Some aspects of the microscopic domains are visible through a microscope, such as a magnified image of graphite or bacteria. Viruses, for instance, are too small to be seen with the naked eye, but when we’re suffering from a cold, we’re reminded of how real they are.

However, most of the subjects in the microscopic domain of chemistry—such as atoms and molecules—are too small to be seen even with standard microscopes and often must be pictured in the mind. Other components of the microscopic domain include ions and electrons, protons and neutrons, and chemical bonds, each of which is far too small to see. This domain includes the individual metal atoms in a wire, the ions that compose a salt crystal, the changes in individual molecules that result in a colour change, the conversion of nutrient molecules into tissue and energy, and the evolution of heat as bonds that hold atoms together are created.

The **symbolic domain** contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs and drawings. We can also consider calculations as part of the symbolic domain. These symbols play an important role in chemistry because they help interpret the behaviour of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behaviour in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures, will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures (Figure 1.1d) are macroscopic observations. But some properties of water fall into the microscopic domain—what we cannot observe with the naked eye. The description of water as comprised of two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (g) for gas, (s) for solid, and (l) for liquid are also symbolic.

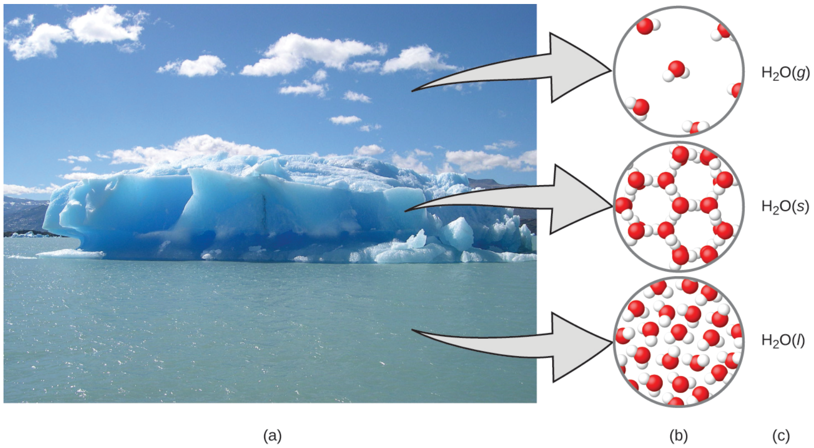

Figure 1.1d (a) Moisture in the air, icebergs and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds are actually comprised of either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit: modification of work by Gorkaazk, CC BY 3.0; in *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 1.1a

Check Your Learning Exercise (Text Version)
Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties. Identify this statement as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

Check Your Answer[1]

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Exercise 1.1b

Check Your Learning Exercise (Text Version)
At a higher temperature, solids (such as salt or sugar) will dissolve better in water. Identify this statement as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

Check Your Answer[2]

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Exercise 1.1c

Check Your Learning Exercise (Text Version)
Identify the item in bold (also marked with an *) as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

a. A certain molecule contains one ***H** atom and one Cl atom.
b. ***Copper *wire** has a density of about 8 g/cm3
c. The bottle contains 15 grams of ***Ni *powder**.
d. A ***sulfur *molecule** is composed of eight sulfur atoms.

Check Your Answer[3]

Source: "Exercise 1.1c" is adapted from "Exercise 1.1-5c" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Scientists in Action: George Washington Carver, PhD.

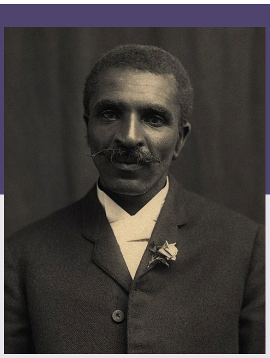

Figure 1.1e George Washington Carver (credit: Photo by Unknown, restored by Adam Cuerden, PD)

George Washington Carver was born into slavery in Missouri. His interest in science started with taking care of plants at a young age. He is most famous for his contributions to agricultural chemistry, and he is credited with developing over 100 uses for the peanut. He was the first African American to have a national monument dedicated to him. The American Chemical Society dedicated his work as a National Historic Chemical Landmark in 2005.Learn more about Dr. George Washington Carver in this American Chemical Society Commemorative booklet [New Tab][PDF]He was dedicated to the continuing education of poor farmers and took his Jessup wagon (think of it as a traveling lab) around to rural communities to share what he had learned. His epitaph reads "He could have added fortune to fame, but caring for neither, he found happiness and honour in being helpful to the world." If you'd like to, listen to an old audio recording of George Washington Carver [New Tab].

Attribution & References

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Notes

1. hypothesis (a tentative explanation, can be investigated by experimentation)
2. theory (a widely accepted explanation of the behaviour of matter);
3. (a) Symbolic, Microscopic; (b) Macroscopic; (c) Symbolic, Macroscopic; (d) Microscopic

1.2 PHASES AND CLASSIFICATION OF MATTER

Learning Objectives

By the end of this section, you will be able to:

- Describe the basic properties of each physical state of matter: solid, liquid, and gas
- Define and give examples of atoms and molecules
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition
- Distinguish between mass and weight
- Apply the law of conservation of matter

Matter is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure 1.2a, Table 1.2a). A **solid** is rigid and possesses a definite shape. A **liquid** flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A **gas** takes both the shape and volume of its container.

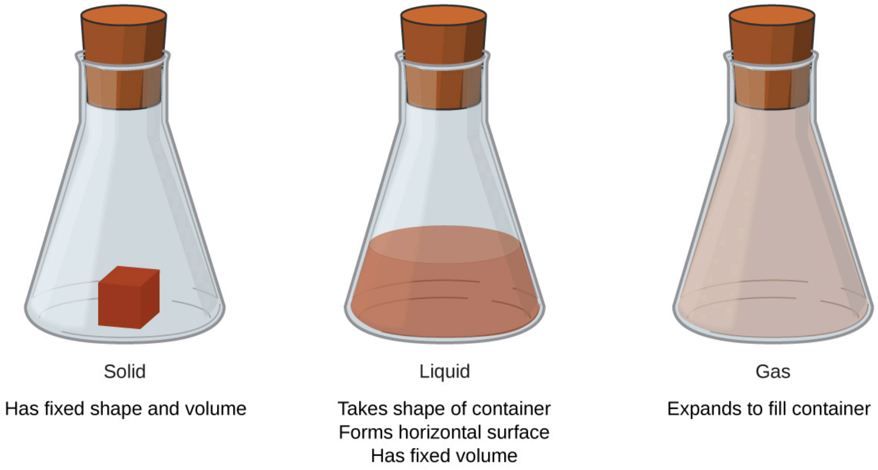

Figure 1.2a The three most common states or phases of matter are solid, liquid, and gas. (credit: [Chemistry (OpenStax)](), [CC BY 4.0]()).

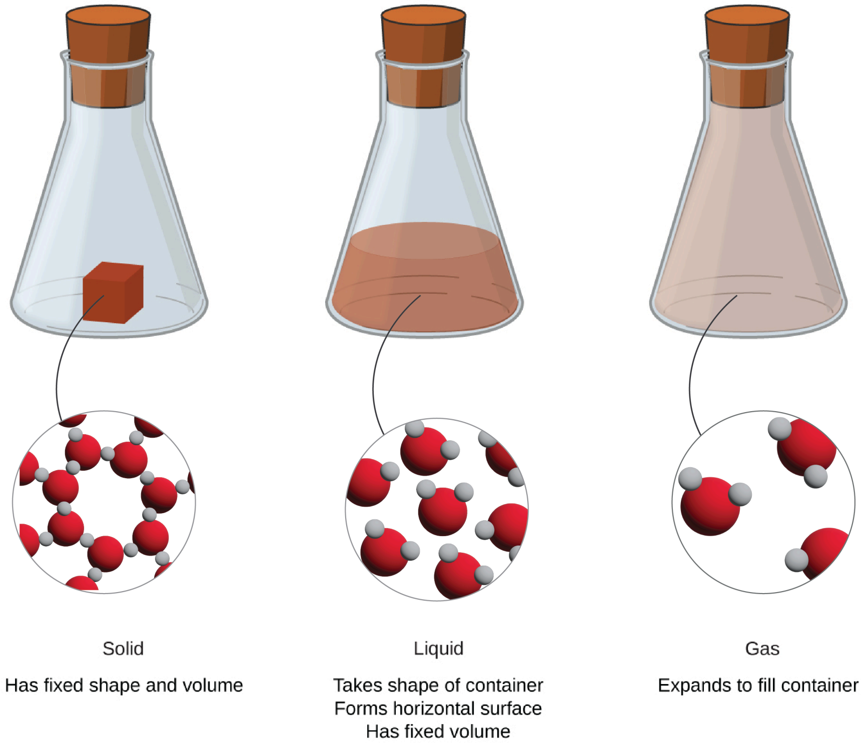

Figure 1.2b States of matter illustrated with the molecular structure of each. (credit: *Chemistry (Open Stax)*, Adapted by Revathi Mahadevan, CC BY 4.0)

Table 1.2a Summary characteristics of the states of matter

Characteristic	Solid	Liquid	Gas
Shape	definite shape	Takes the shape of the container	Takes the shape of the container
Volume	Has a definite volume	Has a definite volume	Fills the volume of the container
Particle Arrangement	Very close, fixed positions	Close, random motion	Far apart, random motion
Particle Interaction	Very strong	Strong	Essentially none
Particle Movement	Very slow	Moderate	Very fast
Examples	Ice, sugar, copper	Water, mercury, ethanol	Water vapour, hydrogen, air

Exercise 1.2a

Check Your Learning Exercise (Text Version)
For each statement, determine whether it is describing a property of a solid, liquid, or gas.

a. cannot be compressed or poured.
b. can be compressed and flow when poured.
c. cannot be compressed, but can be poured.

Check Your Answer[1]

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The fourth state of matter, plasma, occurs naturally in the interiors of stars. A **plasma** is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure 1.2c). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.

Figure 1.2c A plasma torch can be used to cut metal. (credit: work by Hypertherm, undeclared license)

Watch The Chemistry of Light (2006): Silver Chloride Photography (2 mins)

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The **mass** of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. **Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon's gravity is only one-sixth that of the earth's. She may feel "weightless" during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never "massless."

The **law of conservation of matter** summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure 1.2d). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavouring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.

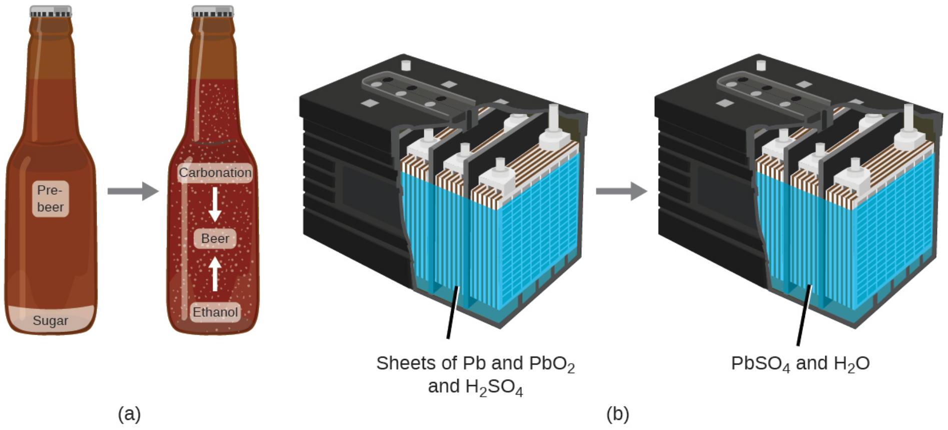

Figure 1.2d (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

Exercise 1.2b

Check Your Learning Exercise (Text Version)
The pressure of a sample of gas is directly proportional to the temperature of the gas. Identify this statement as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

Check Your Answer[2]

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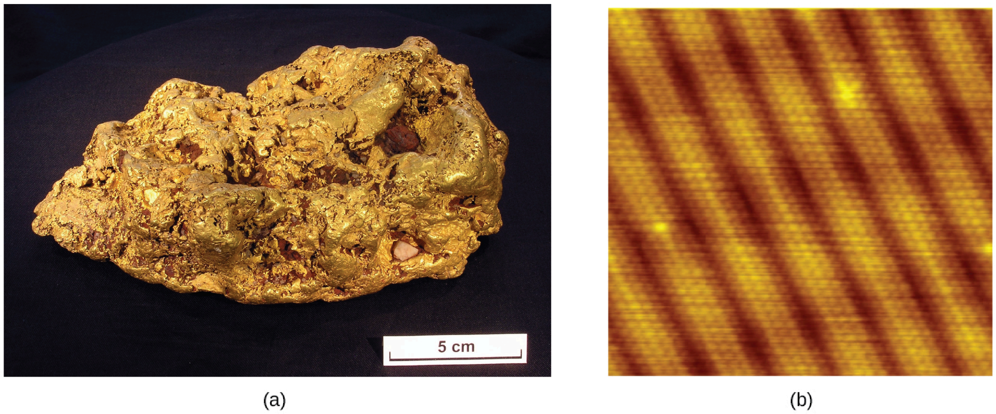
Atoms and Molecules

An **atom** is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning "indivisible") (Figure 1.2e). This atom would no longer be gold if it were divided any further.



(a)

(b)

Figure 1.2e (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by CSIRO, CC BY 3.0; credit b: modification of work by Erwinrossen, PD.)

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry. Other aspects of Dalton's atomic theory are still used but with minor revisions (details of Dalton's theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimetre (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimetre, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom "dimes" to cover it. Figure 1.2f shows increasingly close microscopic and atomic-level views of ordinary cotton.

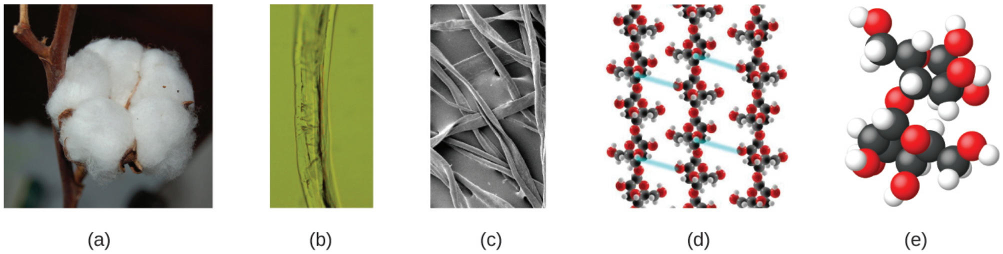


Figure 1.2f These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fibre viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fibre obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fibre (spheres of different colours represent atoms of different elements). (credit a: work by KoS, PD; credit c: modification of work by Featheredtar, CC BY 3.0)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about 3×10^{-13} grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or 3×10^{14}) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms (Figure 1.2g). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A **molecule** consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.

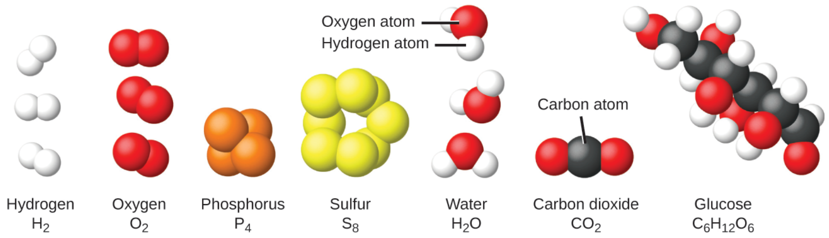


Figure 1.2g The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 1.2c

Check Your Learning Exercise (Text Version)
Fill in the blanks with either "one" or "two or more" to make the statement correct.

a. Molecules of elements contains [BLANK] type(s) of atom(s)?
b. Molecules of compounds contains [BLANK] type(s) of atom(s)?
c. Molecules of elements and molecules of compounds are similar in that both are comprised of [BLANK] atom(s) chemically bonded together.

Check Your Answer[3]

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Exercise 1.2d

Practice using the following PhET simulation: States of Matter

Classifying Matter

We can classify matter into several categories. Two broad categories are mixtures and pure substances. A **pure substance** has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, colour, and sweetness, regardless of the source from which it is isolated.

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called **elements**. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called **compounds**. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen (Figure 1.2h). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).

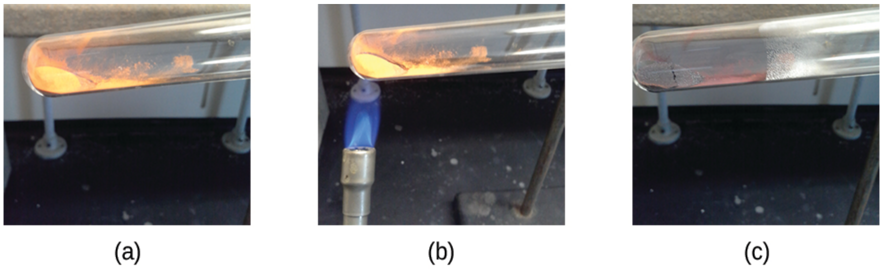

Figure 1.2h (a) The compound mercury(II) oxide, (b) when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers in *Chemistry (OpenStax)*, CC BY 4.0).

Watch Decomposition Mercury (II) Oxide and Oxygen (2 mins)

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colourless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A **mixture** is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a **heterogeneous mixture**. Italian dressing is an example of a heterogeneous mixture (Figure 1.2i). Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A **homogeneous mixture**, also called a **solution**, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, colouring, flavouring, and electrolytes mixed together uniformly (Figure 1.2i). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavouring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.

Figure 1.2i (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a "left": modification of work by John Mayer, CC BY 2.0; credit a "right": modification of work by Umberto Salvagnin, CC BY 2.0; credit b: left: modification of work by Jeff Bedford in *Chemistry (OpenStax)*, CC BY 4.0).

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties by which we can distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in (Figure 1.2j).

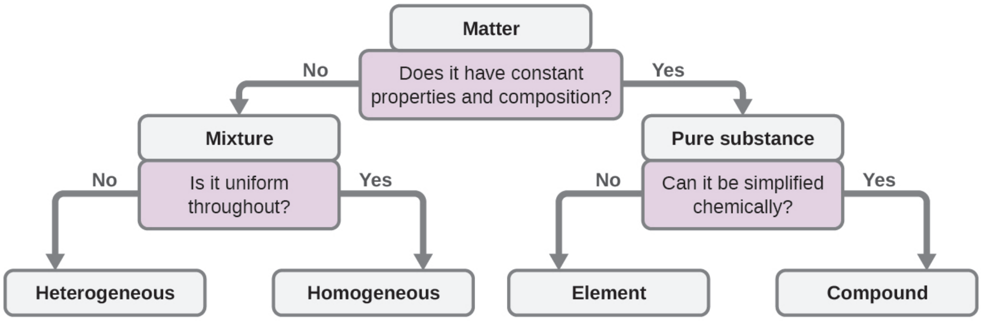

Figure 1.2j Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Eleven elements make up about 99% of the earth's crust and atmosphere (Table 1.2b). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Table 1.2b Elemental Composition of Earth

Element	Symbol	Percent Mass
oxygen	O	49.20
silicon	Si	25.67
aluminum	Al	7.50
iron	Fe	4.71
calcium	Ca	3.39
sodium	Na	2.63
potassium	K	2.40
magnesium	Mg	1.93
hydrogen	H	0.87
titanium	Ti	0.58
chlorine	Cl	0.19
phosphorus	P	0.11
manganese	Mn	0.09
carbon	C	0.08
sulfur	S	0.06
barium	Ba	0.04
nitrogen	N	0.03
fluorine	F	0.03
strontium	Sr	0.02
all others	–	0.47

Exercise 1.2e

Check Your Learning Exercise (Text Version)
Classify each of the following as an element, a compound, or a mixture:

a. iron

b. oxygen
c. mercury oxide
d. pancake syrup
e. carbon dioxide
f. a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom
g. baking soda
h. baking powder

Check Your Answer[4]

Source: “Exercise 1.2e” is adapted from “Exercise 1.2-10” from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in (Figure 1.2k).

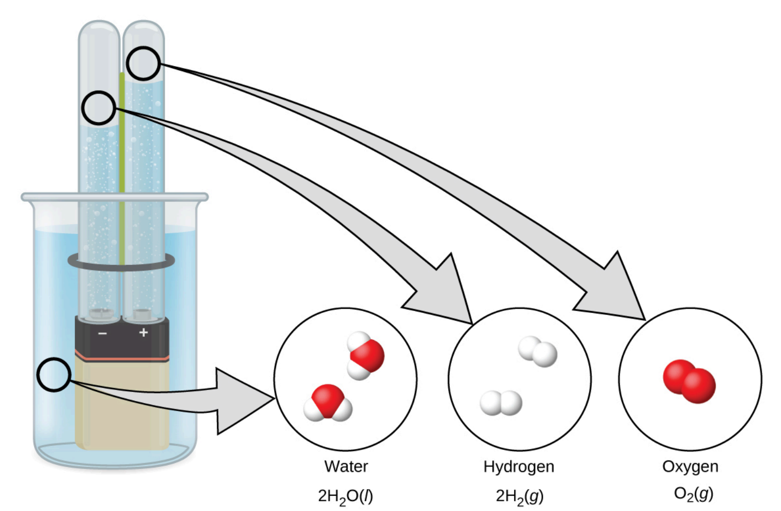

Figure 1.2k The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$, will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline (Figure 1.2l). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.

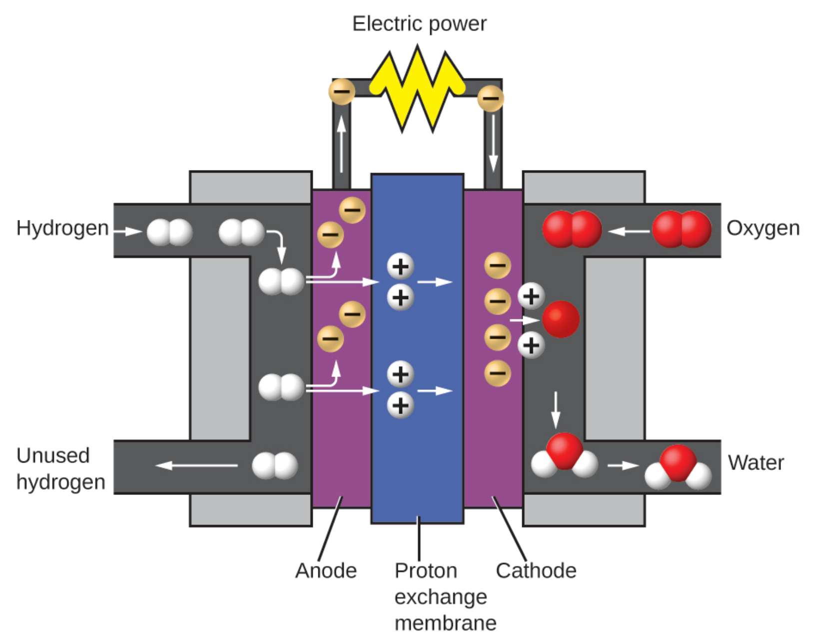

Figure 1.2l A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 1.2f

Check Your Learning Exercise (Text Version)
Guess the answer:

a. Anything that occupies space
b. A measure of the amount of matter contained in an object
c. A measure of the force of gravity acting upon an object
d. The smallest piece of matter that naturally exist
e. Loss of electrons resulting in a positive charge
f. Gain of electrons resulting in a negative charge
g. Are the combination of 2 or more atoms
h. The atoms in a molecule are held together by a

Check Your Answer[5]

Source: "Exercise 1.2f" by Daryl Shaun Aranha is adapted from "1.2 Phases and Classification of Matter" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure 1.2m) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.

Figure 1.2m Almost one-third of naturally occurring elements are used to make a cell phone. (credit: modification of work by John Taylor, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).

Links to Interactive Learning Tools

Explore the Classification of Matter from the Physics Classroom.

Explore Classifying Matter from eCampusOntario H5P Studio.

Attribution & References

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Notes

1. a) solid; b) gas; c) liquid
2. law (states a consistently observed phenomenon, can be used for prediction)
3. (a) one; (b) two or more; (c) two or more
4. (a) element; (b) element; (c) compound; (d) mixture; (e) compound; (f) compound; (g) compound; (h) mixture
5. (a) Matter; (b) Mass; (c) Weight; (d) Atoms; (e) Cation; (f) Anion; (g) Molecules; (h) Chemical Bond

CHAPTER 1 - SUMMARY

1.1 Chemistry in Context

Chemistry deals with the composition, structure, and properties of matter, and the ways by which various forms of matter may be interconverted. Thus, it occupies a central place in the study and practice of science and technology. Chemists use the scientific method to perform experiments, pose hypotheses, and formulate laws and develop theories, so that they can better understand the behaviour of the natural world. To do so, they operate in the macroscopic, microscopic, and symbolic domains. Chemists measure, analyze, purify, and synthesize a wide variety of substances that are important to our lives.

1.2 Phases and Classification of Matter

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

Attributions & References

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CHAPTER 1 - REVIEW

1.1 Chemistry in Context

1. Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer. **Check Answer:** [1]
2. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.
   a. Falling barometric pressure precedes the onset of bad weather.
   b. All life on earth has evolved from a common, primitive organism through the process of natural selection.
   c. My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.
3. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.
   a. The pressure of a sample of gas is directly proportional to the temperature of the gas.
   b. Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.
   c. At a higher temperature, solids (such as salt or sugar) will dissolve better in water.
   Check Answer: [2]
4. Identify each of the following bolded items (also preceded by *) as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.
   a. The mass of a ***lead pipe** is 14 lb.
   b. The mass of a certain ***chlorine atom** is 35 amu.
   c. A bottle with a label that reads ***Al** contains aluminum metal.
   d. ***Al** is the symbol for an aluminum atom.
5. Identify each of the following bolded items (also preceded by *) as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.
   a. A certain molecule contains one ***H** atom and one Cl atom.
   b. ***Copper wire** has a density of about 8 g/cm^3.
   c. The bottle contains 15 grams of ***Ni powder**.
   d. A ***sulfur molecule** is composed of eight sulfur atoms.
   Check Answer: [3]

6. According to one theory, the pressure of a gas increases as its volume decreases because the molecules in the gas have to move a shorter distance to hit the walls of the container. Does this theory follow a macroscopic or microscopic description of chemical behaviour? Explain your answer.
7. The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behaviour? Explain your answer. **Check Answer:** [4]

1.2 Phases and Classification of Matter

1. Why do we use an object's mass, rather than its weight, to indicate the amount of matter it contains?
2. What properties distinguish solids from liquids? Liquids from gases? Solids from gases? **Check Answer:** [5]
3. How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?
4. How does a homogeneous mixture differ from a pure substance? How are they similar? **Check Answer:** [6]
5. How does an element differ from a compound? How are they similar?
6. How do molecules of elements and molecules of compounds differ? In what ways are they similar? **Check Answer:** [7]
7. How does an atom differ from a molecule? In what ways are they similar?
8. Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds. **Check Answer:** [8]
9. Classify each of the following as an element, a compound, or a mixture:
    a. copper
    b. water
    c. nitrogen
    d. sulfur
    e. air
    f. sucrose
    g. a substance composed of molecules each of which contains two iodine atoms
    h. gasoline
10. Classify each of the following as an element, a compound, or a mixture:
    a. iron
    b. oxygen
    c. mercury oxide
    d. pancake syrup
    e. carbon dioxide
    f. a substance composed of molecules each of which contains one hydrogen atom and one chlorine

    atom
   g. baking soda
   h. baking powder
   Check Answer: [9]

11. A sulfur atom and a sulfur molecule are not identical. What is the difference?
12. How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ? **Check Answer:** [10]
13. We refer to astronauts in space as weightless, but not without mass. Why?
14. As we drive an automobile, we don't think about the chemicals consumed and produced. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile. **Check Answer:** [11]
15. Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.
16. When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide which we call rust.
    a. If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain.
    b. If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?
    Check Answer: [12]
17. As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:
    a. Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.
    b. When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.
    c. Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?
18. Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

$$\text{glucose} \rightarrow \text{ethanol} + \text{carbon dioxide}$$

a. If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?

b. If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.

c. If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?
Check Answer: [13]

Attributions & References

Except where otherwise noted, this page is adapted by JR van Haarlem from "1.1 Chemistry in Context" and "1.2 Phases and Classification of Matter" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* / Summary and exercises from the two sections combined into review for our version.

Notes

1. Place a glass of water outside. It will freeze if the temperature is below 0 °C.
2. (a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behaviour of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)
3. (a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic
4. Macroscopic. The heat required is determined from macroscopic properties.
5. Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.
6. The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.
7. Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.
8. Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.
9. (a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture
10. In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.
11. Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.
12. (a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the

mass. (b) 0.9 g

13. (a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

CHAPTER 2. UNDERSTANDING MEASUREMENT

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

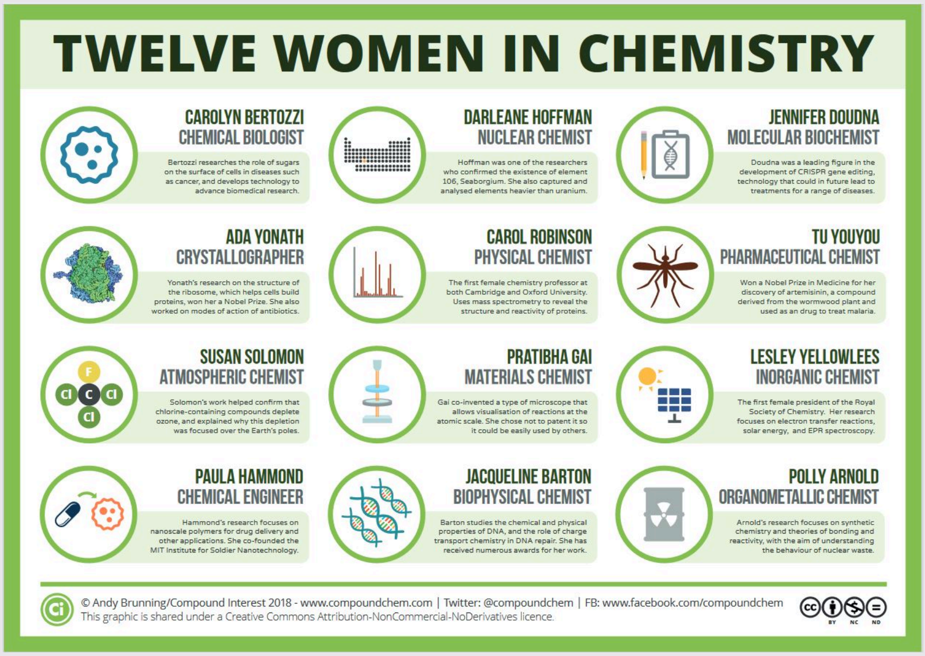
- Exact and uncertain measurements
- Numerical prefixes and equalities
- Analyzing numerical problems

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- The metric system
- Basics of arithmetic

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behaviour of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

Scientists in Action: Twelve Women in Chemistry



CAROLYN BERTOZZI
CHEMICAL BIOLOGIST
Bertozzi researches the role of sugars on the surface of cells in diseases such as cancer, and develops technology to advance biomedical research.

DARLEANE HOFFMAN
NUCLEAR CHEMIST
Hoffman was one of the researchers who confirmed the existence of element 106, Seaborgium. She also captured and analysed elements heavier than uranium.

JENNIFER DOUDNA
MOLECULAR BIOCHEMIST
Doudna was a leading figure in the development of CRISPR gene editing, technology that could in future lead to treatments for a range of diseases.

ADA YONATH
CRYSTALLOGRAPHER
Yonath's research on the structure of the ribosome, which helps cells build proteins, won her a Nobel Prize. She also worked on modes of action of antibiotics.

CAROL ROBINSON
PHYSICAL CHEMIST
The first female chemistry professor at both Cambridge and Oxford University. Uses mass spectrometry to reveal the structure and reactivity of proteins.

TU YOUYOU
PHARMACEUTICAL CHEMIST
Won a Nobel Prize in Medicine for her discovery of artemisinin, a compound derived from the wormwood plant and used as an drug to treat malaria.

SUSAN SOLOMON
ATMOSPHERIC CHEMIST
Solomon's work helped confirm that chlorine-containing compounds deplete ozone, and explained why this depletion was focused over the Earth's poles.

PRATIBHA GAI
MATERIALS CHEMIST
Gai co-invented a type of microscope that allows visualisation of reactions at the atomic scale. She chose not to patent it so it could be easily used by others.

LESLEY YELLOWLEES
INORGANIC CHEMIST
The first female president of the Royal Society of Chemistry. Her research focuses on electron transfer reactions, solar energy, and EPR spectroscopy.

PAULA HAMMOND
CHEMICAL ENGINEER
Hammond's research focuses on nanoscale polymers for drug delivery and other applications. She co-founded the MIT Institute for Soldier Nanotechnology.

JACQUELINE BARTON
BIOPHYSICAL CHEMIST
Barton studies the chemical and physical properties of DNA, and the role of charge transport chemistry in DNA repair. She has received numerous awards for her work.

POLLY ARNOLD
ORGANOMETALLIC CHEMIST
Arnold's research focuses on synthetic chemistry and theories of bonding and reactivity, with the aim of understanding the behaviour of nuclear waste.

Figure 2a "Twelve Women in Chemistry" by Andy Brunning/Compound Interest is licensed under CC BY-NC-ND 4.0.

Attributions & References

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2.1 MEASUREMENTS

Learning Objectives

By the end of this section, you will be able to:

- Understand and apply fundamental measurements in scientific notation.
- Employ Systeme Internationale (SI) measurements

Scientific Notation

The number in the measurement can be represented in different ways, including decimal form and scientific notation. For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98×10^5 kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as 2.5×10^{-6} kg.

Scientific Notation is a method to simplify very large and very small numbers by utilizing a base 10 exponential methodology. The in above examples given 298 000 kg is equivalent to 2.98 × 10 × 10 × 10 × 10 × 10 × 10 or $2.98{\times}10^5$ whereas, 0.0000025 kilograms, is equivalent to 2.5 × 1/10 × 1/10 × 1/10 × 1/10 × 1/10 × 1/10 or $2.5 \text{ x } 10^{-6}$ kg. Using a scientific calculator effectively can reduce the introduction of calculation errors. For example, 298 000 can be inputted as 2.98 [EXP] 5 as scientific notation of the former example.

Units

Units, such as litres, pounds, and centimetres, are standards of comparison for measurements. When we buy a 2-litre bottle of a soft drink, we expect that the **volume** of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 litre. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient’s seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

We usually report the results of scientific measurements in **SI units**, an updated version of the metric system, using the units listed in Table 2.1a. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the International System of Units or SI Units (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Table 2.1a Base Units of the SI System

Property Measured	Name of Unit	Symbol of Unit
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometre because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometre = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 2.1b.

Table 2.1b Common Unit Prefixes

Prefix	Symbol	Factor	Example
femto	f	10^{-15}	1 femtosec ond (fs) = 1 × 10^{-15} s (0.000000000000001 s)
pico	p	10^{-12}	1 picometer (pm) = 1 × 10^{-12} m (0.000000000001 m)
nano	n	10^{-9}	4 nanograms (ng) = 4 × 10^{-9} g (0.000000004 g)
micro	µ	10^{-6}	1 microliter (µL) = 1 × 10^{-6} L (0.000001 L)
milli	m	10^{-3}	2 millimoles (mmol) = 2 × 10^{-3} mol (0.002 mol)
centi	c	10^{-2}	7 centimeters (cm) = 7 × 10^{-2} m (0.07 m)
deci	d	10^{-1}	1 deciliter (dL) = 1 × 10^{-1} L (0.1 L)
kilo	k	10^{3}	1 kilometer (km) = 1 × 10^{3} m (1000 m)
mega	M	10^{6}	3 megahertz (MHz) = 3 × 10^{6} Hz (3,000,000 Hz)
giga	G	10^{9}	8 gigayears (Gyr) = 8 × 10^{9} yr (8,000,000,000 Gyr)
tera	T	10^{12}	5 terawatts (TW) = 5 × 10^{12} W (5,000,000,000,000 W)

SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

Length

The standard unit of **length** in both the SI and original metric systems is the **meter (m)**. A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure 2.1a); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometres (1 km = 1000 m = 10^{3} m), whereas shorter distances can be reported in centimetres (1 cm = 0.01 m = 10^{-2} m) or millimetres (1 mm = 0.001 m = 10^{-3} m).

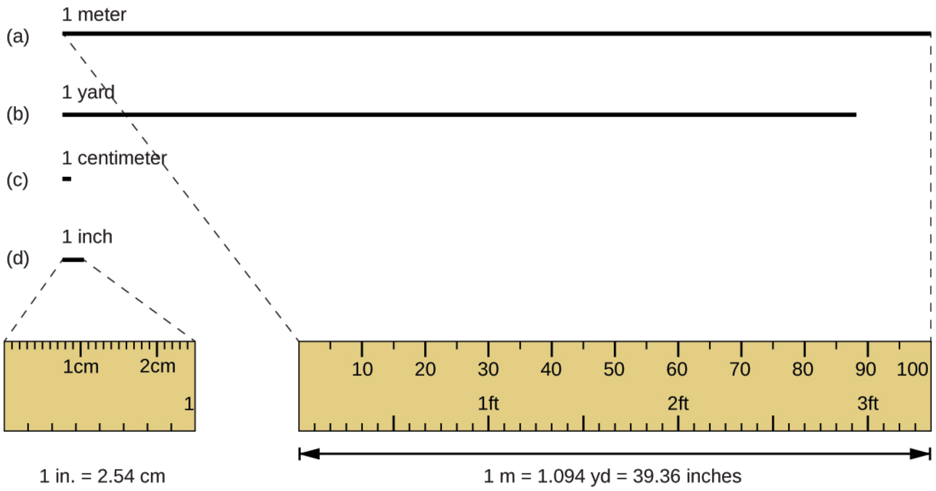


Figure 2.1a The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Mass

The standard unit of mass in the SI system is the **kilogram (kg)**. A kilogram was originally defined as the mass of a litre of water (a cube of water with an edge length of exactly 0.1 meter). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France (Figure 2.1b). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg).

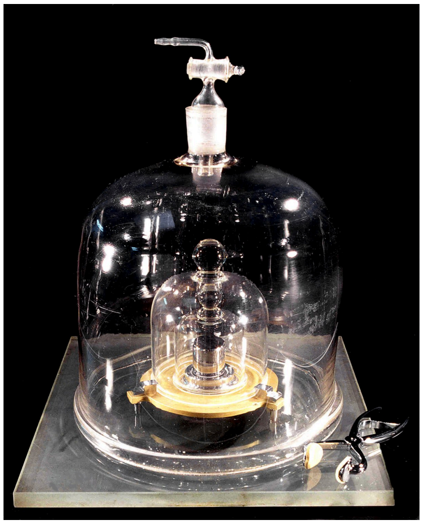
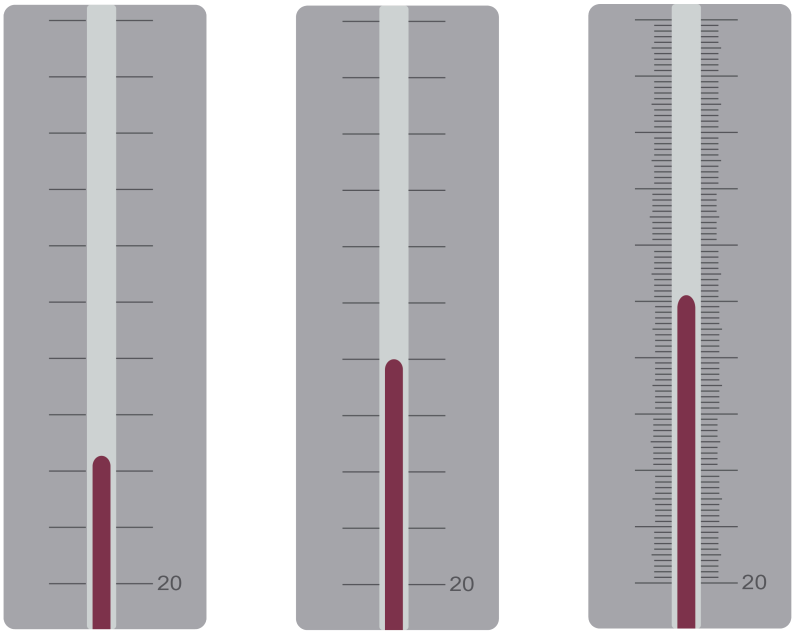


Figure 2.1b This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: photo by BIPM, CC BY-SA 3.0)

Temperature

Temperature is an intensive property. The SI unit of temperature is the **kelvin (K)**. The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word "degree" nor the degree symbol (°). The degree **Celsius (°C)** is also allowed in the SI system, with both the word "degree" and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter. The degree of precision varies when measuring temperature (Figure 2.1c).



23.2°C
Precise to 0.1°C

24°C
Precise to 0.1°C

25.12°C
Precise to 0.01°C

Figure 2.1c Different degrees of precision while measuring temperature. (credit: graphics by Revathi Mahadevan, CC BY 4.0)

Time

The SI base unit of time is the **second (s)**. Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 megaseconds = 5,000,000 s = 5×10^{6} s. Alternatively, hours, days, and years can be used.

Derived SI Units

We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density. Figures 2.1d and 2.1e demonstrate various volumes and masses of cubes.

Figure 2.1d The figure shows 3 cubes. Each of equal volume but with varying masses. (credit: graphics by Revathi Mahadevan, CC BY 4.0)

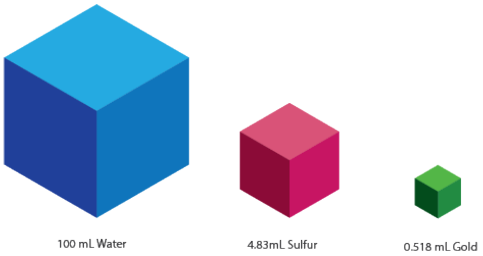


Figure 2.1e The figure shows 3 cubes. Each of equal masses but with varying volumes. (credit: graphics by Revathi Mahadevan, CC BY 4.0)

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 2.1f). The standard volume is a **cubic meter** (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

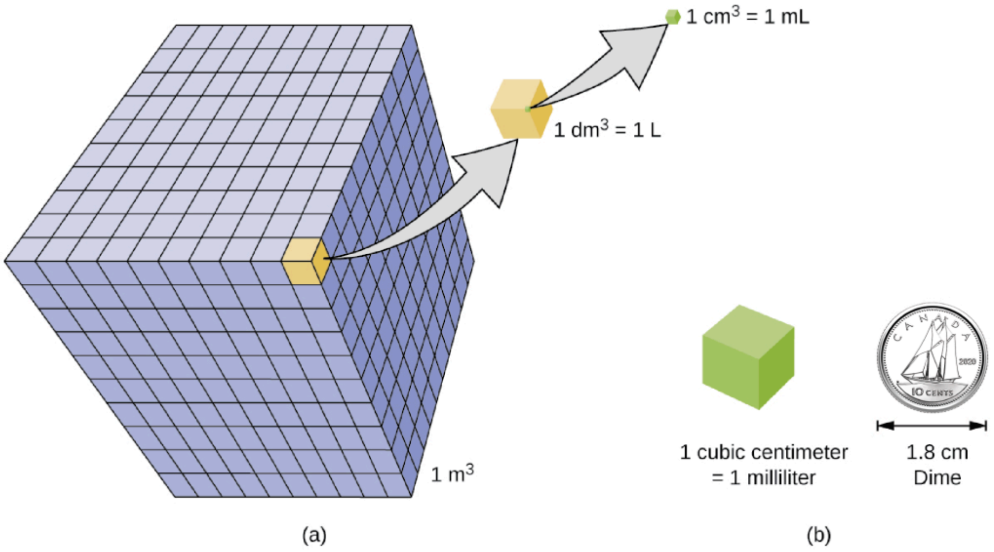


Figure 2.1f (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (credit: *Chemistry 2e (Open Stax)*, CC BY 4.0 . / Canadian dime added by Revathi Mahadevan.)

A more commonly used unit of volume is derived from the decimetre (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimetre contains a volume of one cubic decimetre (dm^3). A **litre (L)** is the more common name for the cubic decimetre. One litre is about 1.06 quarts. A **cubic centimetre** (cm^3) is the volume of a cube with an edge length of exactly one centimetre. The abbreviation **cc** (for **c**ubic **c**entimetre) is often used by health professionals. A cubic centimetre is also called a **millilitre (mL)** and is 1/1000 of a litre.

Density

We use the mass and volume of a substance to determine its **density**. Thus, the units of density are defined by the base units of mass and length.

The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimetre (g/cm^3) for the densities of solids and liquids, and grams per litre (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. Table 2.1c shows the densities of some common substances.

Table 2.1c Densities of Common Substances

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

Watch How taking a bath led to Archimedes' principle – Mark Salata (3 mins)

Example 2.1a

Density of lead

Calculation of Density Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centres of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold, 19.3 g/cm^3. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

$$\text{volume of lead cube} = 2.00\text{cm} \times 2.00\text{cm} \times 2.00\text{cm} = 9.00\text{cm}^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7\text{g}}{8.00\text{cm}^3} = \frac{11.3\text{g}}{1.00\text{cm}^3} = 11.3\ \text{g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

Exercise 2.1a

1. To three decimal places, what is the volume of a cube (cm^3) with an edge length of 0.843 cm?
2. If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?

Check Your Answer[1]

Example 2.1b

Displacement of water to determine density.

The simulation uses the displacement of water to determine the density. In the Compare section, determine the density of the red and yellow blocks.

Practice using the following PhET simulation: Density

Exercise 2.1b

Using the PhET Density simulation in Example 2.1b, remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank. Determine the density of the green block.

Check Your Answer[2]

Exercise 2.1c

Check Your Learning Exercise (Text Version)
For each of the following seven options (a-g), choose an SI base unit or derived unit from the word list that is appropriate for each given measurement:

Word List:

cubic millimeters, kilogram per cubic meter, degree Celsius, kilometer, meter per second, kilograms, square meters.

a. The mass of the moon
b. The distance from Vancouver to Toronto
c. The speed of sound
d. The density of air
e. The temperature at which alcohol boils
f. The area of the province of Newfoundland and Labrador
g. The volume of a flu shot or a measles vaccination

Check Your Answer[3]

Source: "Exercise 2.1c" is adapted from "Exercise 1.4-4" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Links to Interactive Learning Tools

Explore various units of measurement and scientific notation in Measurement and Numbers from the Physics Classroom.

Practice Scientific Notation Identification from eCampusOntario H5P Studio.

Practice Density Calculation #1 from eCampusOntario H5P Studio.

Practice Density Calculation #2 from eCampusOntario H5P Studio.

Key Equations

- $\text{density} = \frac{\text{mass}}{\text{volume}}$

Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem and Samantha Sullivan Sauer from "1.4 Measurements", In *CHEM 2100: General Chemistry I (Mink*) by CSU San Bernardino. / A derivative of *Chemistry 2e (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson is licensed under CC BY 4.0. Access for free at Chemistry 2e (OpenStax) . / Learning objectives updated, custom graphics added.

Notes

1. (1) 0.599cm^3; (2) 8.91 g/cm^3
2. 2.00 kg/L
3. (a) kilograms; (b) meters; (c) meters/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

2.2 MEASUREMENT UNCERTAINTY, ACCURACY, AND PRECISION

Learning Objectives

By the end of this section, you will be able to:

- Define accuracy and precision
- Differentiate between accuracy and precision
- Distinguish exact and uncertain numbers
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an **exact number**. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimetres, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

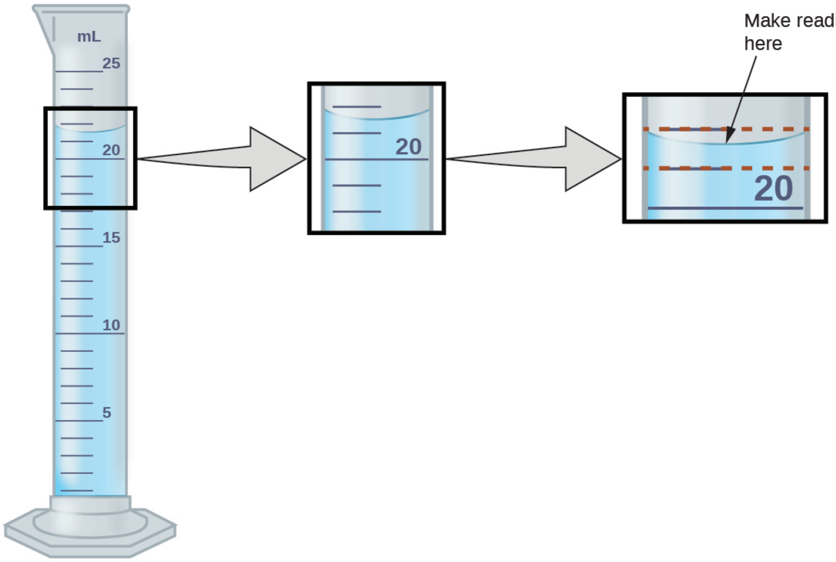


Figure 2.2a To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a millilitre, and then make a reading (estimate) at the bottom of the meniscus (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Refer to the illustration in Figure 2.2a. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If we weigh the quarter on a more sensitive balance, we may find that its mass is 6.723 g. This means its mass lies between 6.722 and 6.724 grams, with an uncertainty of 0.001 grams. Every measurement has some **uncertainty**, which depends on the device used (and the user's ability). All of the digits in measurement, including the uncertain last digit, are called **significant figures** or **significant digits**. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens), and 0 (ones) are all significant (measured) values.

Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them (Figure 2.2b).

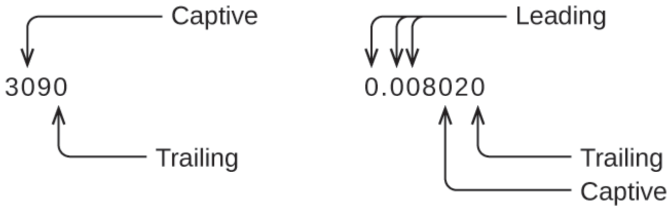


Figure 2.2b Examples of captive, leading and training zeros in multidigit numbers. A captive zero appears between two non-zero digitals. A leading zero appears before any non-zero digits. A trailing zero appears after the last non-zero digit (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point (Figure 2.2c).

Figure 2.2c All non-zero digits are significant. Zeros to the right of a decimal point after a non-zero digit are significant (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located (Figure 2.2d).

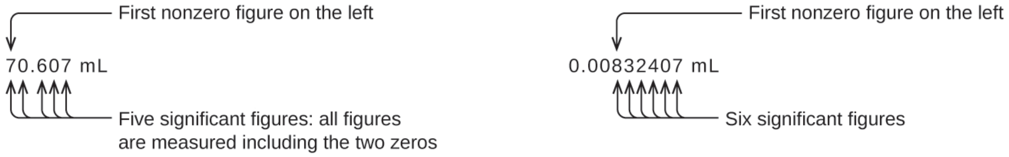


Figure 2.2d Trailing zeros may or may not be significant when there is no decimal. Assume the trailing zeros are not significant when there is no decimal (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The leading zeros in this example are not significant. We could use the exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located (Figure 2.2e). The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the one's place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.

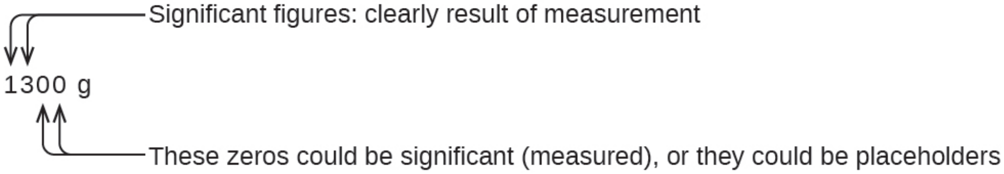


Figure 2.2e The zeros could be significant (measured) or placeholders depending on the measurement (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely when evaluating whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as 3.17×10^8 people.

Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for **rounding** numbers:

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we

“round down” and leave the retained digit unchanged; if it is 5 or more, we “round up” and increase the retained digit by 1.

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds “up” to 0.0287 (the dropped digit, 7, and therefore round up)
- 18.3384 rounds “down” to 18.3 (the dropped digit, 3, and therefore round down)
- 6.8752 rounds “up” to 6.88 (the dropped digit is 5, and therefore round up)

Let’s work through these rules with a few examples.

Example 2.2a

Rounding Numbers

Round the following to the indicated number of significant figures:

a. 31.57 (to two significant figures)
b. 8.1649 (to three significant figures)
c. 0.051065 (to four significant figures)
d. 0.90275 (to two significant figures)

Solution

a. 31.57 rounds “up” to 32 (the dropped digit is 5, and therefore round up)
b. 8.1649 rounds “down” to 8.16 (the dropped digit, 4, and therefore round down)
c. 0.051065 rounds “up” to 0.05107 (the dropped digit is 5, and therefore round up)
d. 0.90275 rounds “down” to 0.90 (the dropped digit is 2, and therefore round down)

Exercise 2.2a

Round the following to the indicated number of significant figures:

a. 0.424 (to two significant figures)
b. 0.0038661 (to three significant figures)
c. 421.25 (to four significant figures)
d. 28,683.5 (to five significant figures)

Check Your Answer[1]

Example 2.2b

Addition and Subtraction with Significant Figures

Rule: When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (i.e., the least precise value in terms of addition and subtraction).

a. Add 1.0023 g and 4.383 g.
b. Subtract 421.23 g from 486 g.

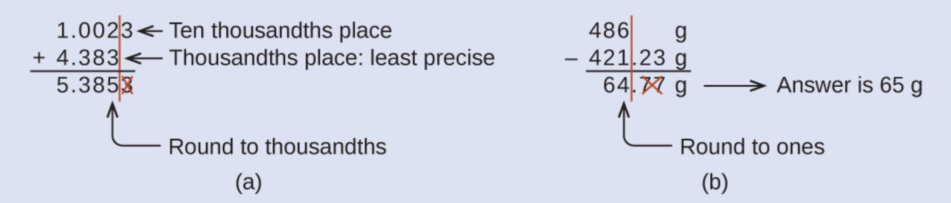
Solution

a.
$$\begin{array}{r} 1.0023\text{g} \\ +4.383\ \ \text{g} \\ \hline 5.3853\text{g} \end{array}$$

Answer is 5.385 g (round to the thousandths place; three decimal places)

b.
$$\begin{array}{r} 486\ \ \ \ \ \text{g} \\ -421.23\text{g} \\ \hline 64.77\text{g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)



Exercise 2.2b

Correctly apply the rules of addition and subtraction with significant figures to perform the following calculations:

a. Add 2.334 mL and 0.31 mL.
b. Subtract 55.8752 m from 56.533 m.

Check Your Answer[2]

Example 2.2c

Multiplication and Division with Significant Figures

Rule: When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).

a. Multiply 0.6238 cm by 6.6 cm.
b. Divide 421.23 g by 486 mL.

Solution

a. 0.6238 cm × 6.6 cm = 4.11708 cm^2 → result is 4.1 cm^2 (round to two significant figures)
four significant figures × two significant figures → two significant figures answer

b. $\frac{421.23\text{g}}{486\text{mL}} = 0.86728\ldots\text{g/mL} \rightarrow \text{result is } 0.867\text{ g/mL (round to three significant figures)}$

$$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow \text{three significant figures answer}$$

Exercise 2.2c

Correctly apply the rules of multiplication and division with significant figures to perform the following calculations:

a. Multiply 2.334 cm and 0.320 cm.
b. Divide 55.8752 m by 56.53 s.

Check Your Answer[3]

In the midst of all these technicalities, it is important to keep in mind the reason why we use significant figures and rounding rules—to correctly represent the certainty of the values we report and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

Example 2.2d

Calculation with Significant Figures

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

Solution

$$\begin{aligned} V = \quad & l \times w \times d \\ & 13.44\text{ dm} \times 5.920\text{ dm} \times 2.54\text{ dm} \\ & 202.09459\ldots\text{ dm}^3 \text{(value from calculator)} \\ & 202\text{ dm}^3,\text{ or } 202\text{ L (answer rounded to three significant figures)} \end{aligned}$$

Exercise 2.2d

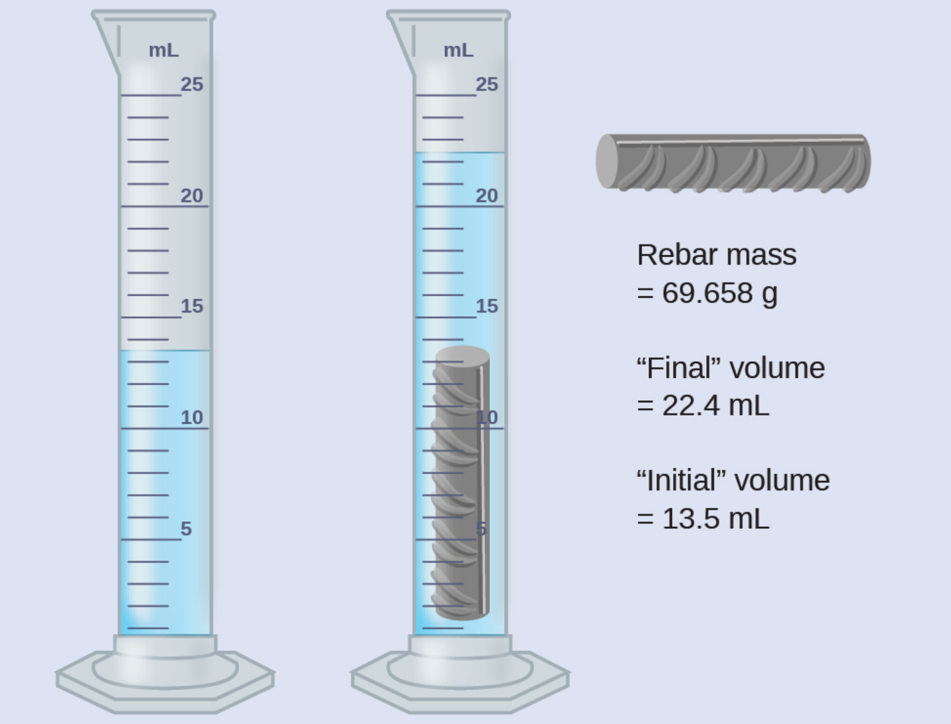
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Check Your Answer[4]

Example 2.2e

Experimental Determination of Density Using Water Displacement

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



a. Use these values to determine the density of this piece of rebar.
b. Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

$$\text{volume} = 22.4\text{mL} - 13.5\text{mL} = 8.9\text{mL} = 8.9\text{cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658\text{g}}{8.9\text{cm}^3} = 7.8\text{g/cm}^3$$

(rounded to two significant figures, per the rule for multiplication and division)

From Table 2.1c, the density of iron is 7.9 g/cm^3, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

Exercise 2.2e

Check Your Learning

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.

a. Use these values to determine the density of this material.
b. Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Check Your Answer[5]

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the **precision** and the **accuracy** of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 2.2f).

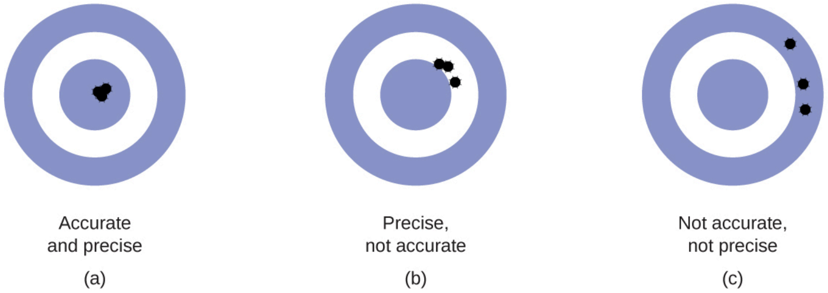


Figure 2.2f (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 2.2a.

Table 2.2a Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Watch What's the difference between accuracy and precision? – Matt Anticole (5 mins).

Links to Interactive Learning Tools

Explore significant digits in Significant Digits and Measurement from the Physics Classroom.

Attribution & References

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Notes

1. (a) 0.42; (b) 0.00387; (c) 421.2; (d) 28,684
2. (a) 2.64 mL; (b) 0.658 m
3. (a) 0.747 cm^2 (b) 0.9884 m/s
4. 1.034 g/mL
5. (a) 19 g/cm^3; (b) It is likely gold; the right appearance for gold and very close to the density given for gold in Table 2.1c.

2.3 MATHEMATICAL TREATMENT OF MEASUREMENT RESULTS

Learning Objectives

By the end of this section, you will be able to:

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities
- Use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:

$$\text{speed} = \frac{\text{distance}}{\text{time}}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of

$$\frac{100\ \text{m}}{10\ \text{s}} = 10\ \text{m/s}$$

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity (100/10 = 10) *and likewise* dividing the units of each measured quantity to yield the unit of the computed quantity (m/s = m/s). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation between the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:

$$\text{time} = \frac{\text{distance}}{\text{speed}}$$

The time can then be computed as:

$$\frac{25\text{ m}}{10\text{ m/s}} = 2.5\text{ s}$$

Again, arithmetic on the numbers (25/10 = 2.5) was accompanied by the same arithmetic on the units (m/m/s = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is "1"—or, as commonly phrased, the units "cancel."

These calculations are examples of a versatile mathematical approach known as **dimensional analysis** (or the **factor-label method**). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

Conversion Factors and Dimensional Analysis

A ratio of two equivalent quantities expressed with different measurement units can be used as a **unit conversion factor**. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

$$\frac{2.54\text{ cm}}{1\text{ in.}}\ (2.54\text{ cm} = 1\text{ in.})\text{ or }2.54\frac{\text{cm}}{\text{in}}$$

Several other commonly used conversion factors are given in Table 2.3a. A more complete list is available in Appendix C.

Table 2.3a Common Conversion Factors

Type of Unit	Unit	Equivalent Unit
length	1 m	1.0936 yd
length	1 in.	2.54 cm (exact)
length	1 km	0.62137 mi
length	1 mi	1609.3 m
volume	1 L	1.0567 qt
volume	1 qt	0.94635 L
volume	1 ft^3	28.317 L
volume	1 tbsp	14.787 mL
mass	1 kg	2.2046 lb
mass	1 lb	453.59 g
mass	1 (avoirdupois) oz	28.349 g
mass	1 (troy) oz	31.103 g

When we multiply a quantity (such as distance given in inches) by an appropriate unit conversion factor, we convert the quantity to an equivalent value with different units (such as distance in centimetres). For example, a basketball player's vertical jump of 34 inches can be converted to centimetres by:

$$34\ \text{in.} \times \frac{2.54\ \text{cm}}{1\ \cancel{\text{in}}} = 86\ \text{cm}$$

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield $\frac{\text{in.} \times \text{cm}}{\text{in.}}$. Just as for numbers, a ratio of identical units is also numerically equal to one, $\frac{\text{in.}}{\text{in.}} = 1$, and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to "cancel.") Using dimensional analysis, we can determine that a unit conversion factor has been set up correctly by checking to confirm that the original unit will cancel, and the result will contain the sought (converted) unit.

Example 2.3a

Using a Unit Conversion Factor

The mass of a competition frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table 2.3a).

Solution

If we have the conversion factor, we can determine the mass in kilograms using an equation similar the one used for converting length from inches to centimetres.

$$x\ \text{oz} = 125\ \text{g} \times \text{unit conversion factor}$$

We write the unit conversion factor in its two forms:

$$\frac{1\ \text{oz}}{28.349\ \text{g}} \text{ and } \frac{28.349\ \text{g}}{1\ \text{oz}}$$

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.

$$x\ \text{oz} = 125\ \cancel{\text{g}} \times \frac{1\ \text{oz}}{28.349\ \cancel{\text{g}}}$$

$$\left(\frac{125}{28.349}\right)\text{oz}$$

$$4.41\ \text{oz (three significant figures)}$$

Exercise 2.3a

Convert a volume of 9.345 qt to litres.

Check Your Answer[1]

Beyond simple unit conversions, the factor-label method can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to insure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. This is why it is referred to as the factor-label method. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example 2.3b

Computing Quantities from Measurement Results and Known Mathematical Relations

What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

Solution

Since density = $\frac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in millilitres. In general: the number of units of B = the number of units of A × unit conversion factor. The necessary conversion factors are given in Table 2.3a: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams in one step:

$$9.26\ \cancel{\text{lb}} \times \frac{453.59\ \text{g}}{1\ \cancel{\text{lb}}} = 4.20 \times 10^3\ \text{g}$$

We need to use two steps to convert volume from quarts to millilitres.

1. *Convert quarts to liters.*

$$4.00\ \cancel{\text{qt}} \times \frac{1\text{L}}{1.0567\cancel{\text{qt}}} = 3.78\text{L}$$

2. *Convert liters to milliliters.*

$$3.78\ \cancel{\text{L}} \times \frac{1000\ \text{L}}{\cancel{\text{L}}} = 3.78\ \text{L} \times 10^3\ \text{mL}$$

Then,

$$\text{density} = \frac{4.20 \times 10^3\ \text{g}}{3.78 \times 10^3\ \text{mL}} = 1.11\ \text{g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:

$$\frac{9.26\cancel{\text{lb}}}{4.00\cancel{\text{qt}}} \times \frac{453.59\text{g}}{1\cancel{\text{L}}} \times \frac{1.0567\cancel{\text{qt}}}{1\cancel{\text{L}}} \times \frac{1\cancel{\text{L}}}{1000\text{mL}} = 1.11\text{g/mL}$$

Exercise 2.3b

What is the volume in litres of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

Check Your Answer[2]

Example 2.3c

Computing Quantities from Measurement Results and Known Mathematical Relations

While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.

- What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?
- If gasoline costs \$3.80 per gallon, what was the fuel cost for this trip?

Solution

1. We first convert distance from kilometres to miles:

$$1250\ \text{km} \times \frac{0.62137\ \text{mi}}{1\ \text{km}} = 777\ \text{mi}$$

and then convert volume from liters to gallons:

$$213\ \cancel{\text{L}} \times \frac{1.0567\ \cancel{\text{qt}}}{1\ \cancel{\text{L}}} \times \frac{1\ \text{gal}}{4\ \cancel{\text{qt}}} = 56.3\ \text{gal}$$

Then,

$$\text{(average) mileage} = \frac{777\ \text{mi}}{56.3\ \text{gal}} = 13.8\ \text{miles/gallon} = 13.8\ \text{mpg}$$

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:

$$\frac{1250\ \cancel{\text{km}}}{213\ \cancel{\text{L}}} \times \frac{0.62137\ \text{mi}}{1\ \cancel{\text{km}}} \times \frac{1\ \cancel{\text{L}}}{1.0567\ \cancel{\text{qt}}} \times \frac{4\ \cancel{\text{qt}}}{1\ \text{gal}} = 13.8\ \text{mpg}$$

2. Using the previously calculated volume in gallons, we find:

$$56.3\ \text{gal} \times \frac{\$3.80}{1\ \text{gal}} = \$214$$

Exercise 2.3c

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

1. What (average) fuel economy, in miles per gallon, did the Prius get during this trip?
2. If gasoline costs \$3.90 per gallon, what was the fuel cost for this trip?

Check Your Answer[3]

Conversion of Temperature Units

We use the word **temperature** to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes. Because the volume of the liquid changes more than the volume of the glass, we can see the liquid expand when it gets warmer and contract when it gets cooler.

To mark a scale on a thermometer, we need a set of reference values: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the **Fahrenheit** scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

Defining the Celsius and Fahrenheit temperature scales as described in the previous paragraph results in a slightly more complex relationship between temperature values on these two scales than for different units of measure for other properties. Most measurement units for a given property are directly proportional to one another (y = mx). Using familiar length units as one example:

$$\text{length in feet} = \left(\frac{1\ \text{ft}}{12\ \text{in.}}\right) \times \text{length in inches}$$

where y = length in feet, x = length in inches, and the proportionality constant, m, is the conversion factor. The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one (y = mx + b). Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor, m, it also must take into account differences in the scales' zero points (b).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as *x* and the Fahrenheit temperature as *y*, the slope, *m*, is computed to be:

$$m = \frac{\Delta y}{\Delta x} = \frac{212\ ^\circ\text{F} - 32\ ^\circ\text{F}}{100\ ^\circ\text{C} - 0\ ^\circ\text{C}} = \frac{180\ ^\circ\text{F}}{100\ ^\circ\text{C}} = \frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}}$$

The y-intercept of the equation, *b*, is then calculated using either of the equivalent temperature pairs, (100 °C, 212 °F) or (0 °C, 32 °F), as:

$$b = y - mx = 32\ ^\circ\text{F} - \frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \times 0\ ^\circ\text{C} = 32\ ^\circ\text{F}$$

The equation relating the temperature scales is then:

$$T_{^\circ\text{F}} = (\frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \times T_{^\circ\text{C}}) + 32\ ^\circ\text{C}$$

An abbreviated form of this equation that omits the measurement units is:

$$T_{^\circ\text{F}} = \frac{9}{5} \times T_{^\circ\text{C}} + 32$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

$$T_{^\circ\text{C}} = \frac{5}{9}(T_{^\circ\text{F}} - 32)$$

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at −273.15 °C. In 1848, British physicist William Thompson, who later adopted the title of Lord Kelvin, proposed an absolute temperature scale based on this concept (further treatment of this topic is provided in this text's chapter on gases).

The freezing temperature of water on this scale is 273.15 K and its boiling temperature 373.15 K. Notice the numerical difference in these two reference temperatures is 100, the same as for the Celsius scale, and so the linear relation between these two temperature scales will exhibit a slope of $1\ \frac{\text{K}}{^\circ\text{C}}$. Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

$$T_{\text{K}} = T_{^\circ\text{C}} + 273.15$$
$$T_{^\circ\text{C}} = T_{\text{K}} - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 2.3a shows the relationship between the three temperature scales. Recall that we do not use the degree sign with temperatures on the Kelvin scale.

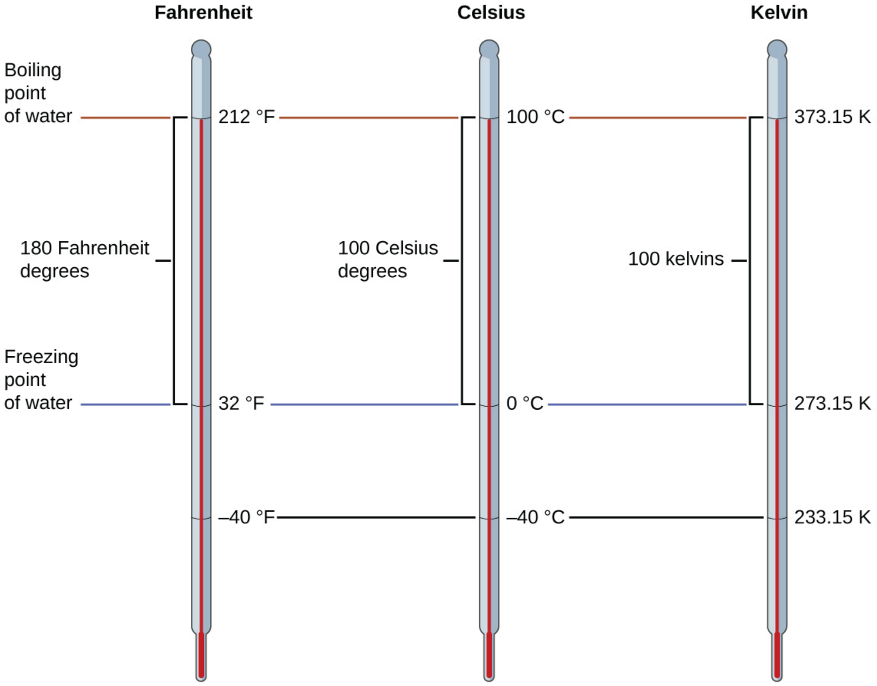


Figure 2.3a The Fahrenheit, Celsius, and kelvin temperature scales are compared.

Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for nonscience contexts in almost all areas of the world. Very few countries (the U.S. and its territories, the Bahamas, Belize, Cayman Islands, and Palau) still use Fahrenheit for weather, medicine, and cooking.

Example 2.3d

Conversion from Celsius

Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the kelvin scale and on the Fahrenheit scale?

Solution

$$\mathrm{K} = ^{\circ}\mathrm{C} + 273.15 = 37.0 + 273.2 = 310.2\ \mathrm{K}$$
$$^{\circ}\mathrm{F} = \frac{9}{5}\,^{\circ}\mathrm{C} + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6^{\circ}\mathrm{F}$$

Exercise 2.3d

Convert 80.92 °C to K and °F.

Check Your Answer[4]

Example 2.3e

Conversion from Fahrenheit

Baking a ready-made pizza calls for an oven temperature of 450 °F. If you are in Europe, and your oven thermometer uses the Celsius scale, what is the setting? What is the kelvin temperature?

Solution

In Celsius:

$$^\circ\text{C} = \frac{5}{9}(^\circ\text{F} - 32) = \frac{5}{9}(450\text{ - }32) = \frac{5}{9} \times 418 = 232\ ^\circ\text{C}$$
$$\longrightarrow \text{set oven to } 230\ ^\circ\text{C(two significant figures)}$$

In kelvin:

$$\text{K} =^\circ \text{C} + 273.15 = 230 + 273 = 503\text{ K}$$
$$\longrightarrow 5.0 \times 10^2\text{K(two significant figures)}$$

Exercise 2.3e

Convert 50 °F to °C and K.

Check Your Answer[5]

Links to Interactive Learning Tools

Explore the Metric System from the Physics Classroom.

Explore Metric Conversions from the Physics Classroom.

Key Equations

- $T_{^\circ\text{C}} = \frac{5}{9} \times T_{^\circ\text{F}} - 32$
- $T_{^\circ\text{F}} = \frac{9}{5} \times T_{^\circ\text{C}} + 32$
- $T_\text{K} = ^\circ\text{C} + 273.15$
- $T_{^\circ\text{C}} = \text{K} - 273.15$

Attributions & References

Except where otherwise noted, this page is adapted by JR van Haarlem from "1.6 Mathematical Treatment of Measurement Results" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*

Notes

1. 8.844 L
2. 2.956 × 10^{-2}L
3. (a) 51 mpg; (b) $62
4. 354.07 K, 177.7 °F
5. 10 °C, 280 K

CHAPTER 2 - SUMMARY

2.1 Measurements

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as litres (for volume) and g/cm^3 (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10^{-6} seconds) and megahertz (10^6 hertz), respectively.

2.2 Measurement Uncertainty, Accuracy, and Precision

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

2.3 Mathematical Treatment of Measurement Results

Measurements are made using a variety of units. It is often useful or necessary to convert a measured quantity from one unit into another. These conversions are accomplished using unit conversion factors, which are derived by simple applications of a mathematical approach called the factor-label method or dimensional analysis. This strategy is also employed to calculate sought quantities using measured quantities and appropriate mathematical relations.

Attributions & References

Except where otherwise noted, this page is adapted by JR van Haarlem from "1.4 Measurements", "1.5 Measurement Uncertainty, Accuracy, and Precision" and "1.6 Mathematical Treatment of Measurement Results" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* . / Reused the summaries from each section to create the chapter summary for this page.

CHAPTER 2 - REVIEW

2.1 Measurements

1. Is one liter about an ounce, a pint, a quart, or a gallon?
2. Is a meter about an inch, a foot, a yard, or a mile?
   Check answers: [1]
3. Indicate the SI base units or derived units that are appropriate for the following measurements:
   a. the length of a marathon race (26 miles 385 yards)
   b. the mass of an automobile
   c. the volume of a swimming pool
   d. the speed of an airplane
   e. the density of gold
   f. the area of a football field
   g. the maximum temperature at the South Pole on April 1, 1913
4. Indicate the SI base units or derived units that are appropriate for the following measurements:
   a. the mass of the moon
   b. the distance from Dallas to Oklahoma City
   c. the speed of sound
   d. the density of air
   e. the temperature at which alcohol boils
   f. the area of the state of Delaware
   g. the volume of a flu shot or a measles vaccination
      Check answers: [2]
5. Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.
   a. 10^3
   b. 10^{-2}
   c. 0.1
   d. 10^{-3}
   e. 1,000,000
   f. 0.000001
6. Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

   a. c
   b. d
   c. G
   d. k
   e. m
   f. n
   g. p
   h. T

   Check answers: [3]

7. A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.
   a. Determine the density of this piece of jewelry.
   b. Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.
8. Visit this density simulation and click the "turn fluid into water" button to adjust the density of liquid in the beaker to 1.00 g/mL.
   a. Use the water displacement approach to measure the mass and volume of the unknown material (select the green block with question marks).
   b. Use the measured mass and volume data from step (a) to calculate the density of the unknown material.
   c. Link out to the link provided.
   d. Assuming this material is a copper-containing gemstone, identify its three most likely identities by comparing the measured density to the values tabulated in this gemstone density guide.
   e. How are mass and density related for blocks of the same volume?

   Check answers: [4]
9. Visit this density simulation and click the "reset" button to ensure all simulator parameters are at their default values.
   a. Use the water displacement approach to measure the mass and volume of the red block.
   b. Use the measured mass and volume data from step (a) to calculate the density of the red block.
   c. Use the vertical green slide control to adjust the fluid density to values well above, then well below, and finally nearly equal to the density of the red block, reporting your observations.
10. Visit this density simulation and click the "turn fluid into water" button to adjust the density of liquid in the beaker to 1.00 g/mL. Change the block material to foam, and then wait patiently until the foam block stops bobbing up and down in the water.
   a. The foam block should be floating on the surface of the water (that is, only partially submerged). What is the volume of water displaced?

   b. Use the water volume from part (a) and the density of water (1.00 g/mL) to calculate the mass of water displaced.
   c. Remove and weigh the foam block. How does the block's mass compare to the mass of displaced water from part (b)? **Check answers:** [5]

2.2 Measurement Uncertainty, Accuracy, and Precision

1. Express each of the following numbers in scientific notation with correct significant figures:
   a. 711.0
   b. 0.03344
   c. 547.9
   d. 22086
   e. 1000.00
   f. 0.0000000651
   g. 0.007157
2. Express each of the following numbers in exponential notation with correct significant figures:
   a. 704
   b. 0.03344
   c. 547.9
   d. 22086
   e. 1000.00
   f. 0.0000000651
   g. 0.007157

   Check answers: [6]
3. Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:
   a. the number of eggs in a basket
   b. the mass of a dozen eggs
   c. the number of gallons of gasoline necessary to fill an automobile gas tank
   d. the number of cm in 2 m
   e. the mass of a textbook
   f. the time required to drive from San Francisco to Kansas City at an average speed of 53 mi/h
4. Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:
   a. the number of seconds in an hour
   b. the number of pages in this book
   c. the number of grams in your weight

   d. the number of grams in 3 kilograms
   e. the volume of water you drink in one day
   f. the distance from San Francisco to Kansas City

   Check answers: [7]

5. How many significant figures are contained in each of the following measurements?
   a. 38.7 g
   b. 2×10^{18} m
   c. 3,486,002 kg
   d. 9.74150×10^{-4} J
   e. 0.0613 cm^3
   f. 17.0 kg
   g. 0.01400 g/mL
6. How many significant figures are contained in each of the following measurements?
   a. 53 cm
   b. 2.05×10^{8} m
   c. 86,002 J
   d. 9.740×10^{4} m/s
   e. 10.0613 m^3
   f. 0.17 g/mL
   g. 0.88400 s

   Check answers: [8]

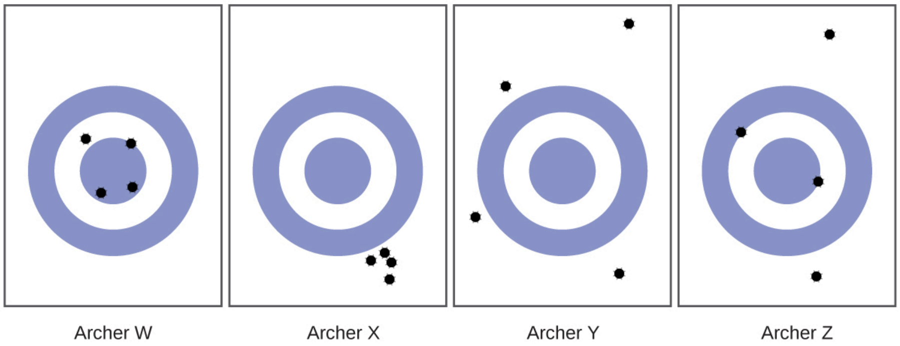
7. The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.
   a. 0.0055 g active ingredients
   b. 12 tablets
   c. 3% hydrogen peroxide
   d. 5.5 ounces
   e. 473 mL
   f. 1.75% bismuth
   g. 0.001% phosphoric acid
   h. 99.80% inert ingredients
8. Round off each of the following numbers to two significant figures:
   a. 0.436
   b. 9.000
   c. 27.2
   d. 135
   e. 1.497×10^{-3}

   f. 0.445

   Check answers: [9]

9. Round off each of the following numbers to two significant figures:
   a. 517
   b. 86.3
   c. 6.382×10^3
   d. 5.0008
   e. 22.497
   f. 0.885
10. Perform the following calculations and report each answer with the correct number of significant figures.
    a. 628 × 342
    b. $(5.63 \times 10^2) \times (7.4 \times 10^3)$
    c. $\frac{28.0}{13.483}$
    d. 8119 × 0.000023
    e. 14.98 + 27,340 + 84.7593
    f. 42.7 + 0.259

    Check answers: [10]
11. Perform the following calculations and report each answer with the correct number of significant figures.
    a. 62.8 × 34
    b. 0.147 + 0.0066 + 0.012
    c. 38 × 95 × 1.792
    d. 15 – 0.15 – 0.6155
    e. $8.78 \times (\frac{0.0500}{0.478})$
    f. 140 + 7.68 + 0.014
    g. 28.7 – 0.0483
    h. $\frac{(88.5 - 87.57)}{45.13}$
12. Consider the results of the archery contest shown in this figure.
    a. Which archer is most precise?
    b. Which archer is most accurate?
    c. Who is both least precise and least accurate?



Check answers: [11]

13. Classify the following sets of measurements as accurate, precise, both, or neither.
    a. Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g
    b. Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL
    c. Determining the purity of gold: 99.9999%, 99.9998%, 99.9998%, 99.9999%

2.3 Mathematical Treatment of Measurement Results

1. Write conversion factors (as ratios) for the number of:
    a. yards in 1 meter
    b. liters in 1 liquid quart
    c. pounds in 1 kilogram
    Check answers: [12]
2. Write conversion factors (as ratios) for the number of:
    a. kilometres in 1 mile
    b. litres in 1 cubic foot
    c. grams in 1 ounce
3. The label on a soft drink bottle gives the volume in two units: 2.0 L and 67.6 fl oz. Use this information to derive a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?
   Check answers: [13]
4. The label on a box of cereal gives the mass of cereal in two units: 978 grams and 34.5 oz. Use this information to find a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?
5. Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimetres and grams?
   Check answers: [14]
6. A woman's basketball has a circumference between 28.5 and 29.0 inches and a maximum weight of 20 ounces (two significant figures). What are these specifications in units of centimetres and grams?

7. How many millilitres of a soft drink is contained in a 12.0-oz can?
   Check answers: [15]
8. A barrel of oil is exactly 42 gal. How many litres of oil are in a barrel?
9. The diameter of a red blood cell is about 3×10^{-4} in. What is its diameter in centimetres?
   Check answers: [16]
10. The distance between the centres of the two oxygen atoms in an oxygen molecule is 1.21×10^{-8} cm. What is this distance in inches?
11. Is a 197-lb weight lifter light enough to compete in a class limited to those weighing 90 kg or less?
    Check answers: [17]
12. A very good 197-lb weight lifter lifted 192 kg in a move called the clean and jerk. What was the mass of the weight lifted in pounds?
13. Many medical laboratory tests are run using 5.0 μL blood serum. What is this volume in millilitres?
    Check answers: [18]
14. If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?
15. Use scientific (exponential) notation to express the following quantities in terms of the SI base units in Table 2.1c in Chapter 2.1 Measurements:
    1. 0.13 g
    2. 232 Gg
    3. 5.23 pm
    4. 86.3 mg
    5. 37.6 cm
    6. 54 μm
    7. 1 Ts
    8. 27 ps
    9. 0.15 mK

       Check answers: [19]
16. Complete the following conversions between SI units.
    a. 612 g = ________ mg
    b. 8.160 m = ________ cm
    c. 3779 μg = ________ g
    d. 781 mL = ________ L
    e. 4.18 kg = ________ g
    f. 27.8 m = ________ km
    g. 0.13 mL = ________ L
    h. 1738 km = ________ m
    i. 1.9 Gg = ________ g
17. Gasoline is sold by the litre in many countries. How many litres are required to fill a 12.0-gal gas tank?

Check answers: [20]

18. Milk is sold by the litre in many countries. What is the volume of exactly 1/2 gal of milk in litres?
19. A long ton is defined as exactly 2240 lb. What is this mass in kilograms?

Check answers: [21]

20. Make the conversion indicated in each of the following:
    a. the men's world record long jump, 29 ft 4¼ in., to meters
    b. the greatest depth of the ocean, about 6.5 mi, to kilometres
    c. the area of the state of Oregon, 96,981 mi^2, to square kilometres
    d. the volume of 1 gill (exactly 4 oz) to millilitres
    e. the estimated volume of the oceans, 330,000,000 mi^3, to cubic kilometres.
    f. the mass of a 3525-lb car to kilograms
    g. the mass of a 2.3-oz egg to grams
21. Make the conversion indicated in each of the following:
    a. the length of a soccer field, 120 m (three significant figures), to feet
    b. the height of Mt. Kilimanjaro, at 19,565 ft the highest mountain in Africa, to kilometres
    c. the area of an 8.5 t 11-inch sheet of paper in cm^2
    d. the displacement volume of an automobile engine, 161 $in.^3$, to litres
    e. the estimated mass of the atmosphere, 5.6 t 10^{15} tons, to kilograms
    f. the mass of a bushel of rye, 32.0 lb, to kilograms
    g. the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)

    Check answers: [22]

22. Many chemistry conferences have held a 50-Trillion Angstrom Run (two significant figures). How long is this run in kilometres and in miles? (1 Å = 1×10^{-10} m)
23. A chemist's 50-Trillion Angstrom Run would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? (1 Å = 1×10^{-8} cm)

Check answers: [23]

24. The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is 0.8206 g/mL, determine the mass in kilograms and pounds of the fuel in a full tank.
25. As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?

Check answers: [24]

26. To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing 1/4 lb is available. Did the student have enough of the compound?
27. A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?

Check answers: [25]

28. In a recent Grand Prix, the winner completed the race with an average speed of 229.8 km/h. What was his speed in miles per hour, meters per second, and feet per second?
29. Solve these problems about lumber dimensions.
    a. To describe to a European how houses are constructed in the US, the dimensions of "two-by-four" lumber must be converted into metric units. The thickness × width × length dimensions are 1.50 in. × 3.50 in. × 8.00 ft in the US. What are the dimensions in cm × cm × m?
    b. This lumber can be used as vertical studs, which are typically placed 16.0 in. apart. What is that distance in centimetres?
    Check answers: [26]
30. The mercury content of a stream was believed to be above the minimum considered safe—1 part per billion (ppb) by weight. An analysis indicated that the concentration was 0.68 parts per billion. What quantity of mercury in grams was present in 15.0 L of the water, the density of which is 0.998 g/ml? ($1\ \text{ppb\textbackslash;Hg} = \dfrac{1\ \text{ng Hg}}{1\ \text{g water}}$)
31. Calculate the density of aluminum if 27.6 cm^3 has a mass of 74.6 g.
    Check answers: [27]
32. Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm^3?
33. Calculate these masses.
    a. What is the mass of 6.00 cm^3 of mercury, density = 13.5939 g/cm^3?
    b. What is the mass of 25.0 mL octane, density = 0.702 g/cm^3?
    Check answers: [28]
34. Calculate these masses.
    a. What is the mass of 4.00 cm^3 of sodium, density = 0.97 g/cm^3 ?
    b. What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?
35. Calculate these volumes.
    a. What is the volume of 25 g iodine, density = 4.93 g/cm^3?
    b. What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?
    Check answers: [29]
36. Calculate these volumes.
    a. What is the volume of 11.3 g graphite, density = 2.25 g/cm^3?
    b. What is the volume of 39.657 g bromine, density = 2.928 g/cm^3?
37. Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.
    Check answers: [30]
38. Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.
39. Convert the temperature of the coldest area in a freezer, −10 °F, to degrees Celsius and kelvin.
    Check answers: [31]

40. Convert the temperature of dry ice, −77 °C, into degrees Fahrenheit and kelvin.
41. Convert the boiling temperature of liquid ammonia, −28.1 °F, into degrees Celsius and kelvin.
    Check answers: [32]
42. The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?
43. The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45 °C. What was the temperature on the Fahrenheit scale?
    Check answers: [33]

Attribution & References

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Notes

1. about a yard
2. (a) kilograms; (b) meters; (c) meters/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters
3. (a) centi-, X 10^{-2}; (b) deci-, X 10^{-1}; (c) Giga-, X 10^{9}; (d) kilo-, X 10^{3}; (e) milli-, X 10^{-3}; (f) nano-, X 10^{-9}; (g) pico-, X 10^{-12}; (h) tera-, X 10^{12}
4. (a) m = 18.58 g, V = 5.7 mL. (b) d = 3.3 g/mL (c) dioptase (copper cyclosilicate, d = 3.28—3.31 g/mL); malachite (basic copper carbonate, d = 3.25—4.10 g/mL); Paraiba tourmaline (sodium lithium boron silicate with copper, d = 2.82—3.32 g/mL)
5. (a) $V_{\text{without block}}$= 25.5 mL, $V_{\text{with block}}$=28.3 mL, $V_{\text{displaced}}$=2.8 mL (b) m_{water} = d x V = 2.8 g/mL (c) $m_{\text{foam block}}$=2.76 g (same as mass of water displaced)
6. (a) 7.04 × 10^2; (b) 3.344 × 10^−2; (c) 5.479 × 10^2; (d) 2.2086 × 10^4; (e) 1.00000 × 10^3; (f) 6.51 × 10^−8; (g) 7.157 × 10^−3
7. (a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain
8. (a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five
9. (a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5 × 10^−3; (f) 0.44
10. (a) 2.15 × 10^5; (b) 4.2 × 10^6; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0
11. (a) Archer X; (b) Archer W; (c) Archer Y
12. (a) 1.0936 yd m^{-1} ; (b) 0.94635 L qt^{-1} ; (c) 2.2046 lb kg^{-1}
13. 2.0 L (67.6 fl oz)-1=0.030 L (1 fl oz)-1
14. 68–71 cm; 400–450 g

15. 355 mL
16. 8×10^{-4} cm
17. yes; weight = 89.4 kg
18. 5.0×10^{-3} mL
19. (a) 1.3×10^{-4} kg; (b) 2.32×10^{8} kg; (c) 5.23×10^{-12} m; (d) 8.63×10^{-5} kg; (e) 3.76×10^{-1} m; (f) 5.4×10^{-5} m; (g) 1×10^{12} s; (h) 2.7×10^{-11} s; (i) 1.5×10^{-4} K
20. 45.4 L
21. 1.0160×10^{3} kg
22. (a) 394 ft; (b) 5.9634 km; (c) 6.0×10^{2}; (d) 2.64 L; (e) 5.1×10^{18} kg; (f) 14.5 kg; (g) 324 mg
23. 0.46 m; 1.5 ft/cubit
24. Yes, the acid's volume is 123 mL.
25. 62.6 in (about 5 ft 3 in.) and 101 lb.
26. (a) 3.81 cm × 8.89 cm × 2.44 m; (b) 40.6 cm
27. 2.70 g/cm^3
28. (a) 81.6 g; (b) 17.6 g
29. (a) 5.1 mL; (b) 37 L
30. 5371 °F, 3239 K
31. −23 °C, 250 K
32. −33.4 °C, 239.8 K
33. 113 °F

CHAPTER 3. BUILDING BLOCKS OF MATTER

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- Elements and ions
- Chemical symbols
- The periodic table
- Ionic and molecular compounds
- Chemical formulas

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Numeracy

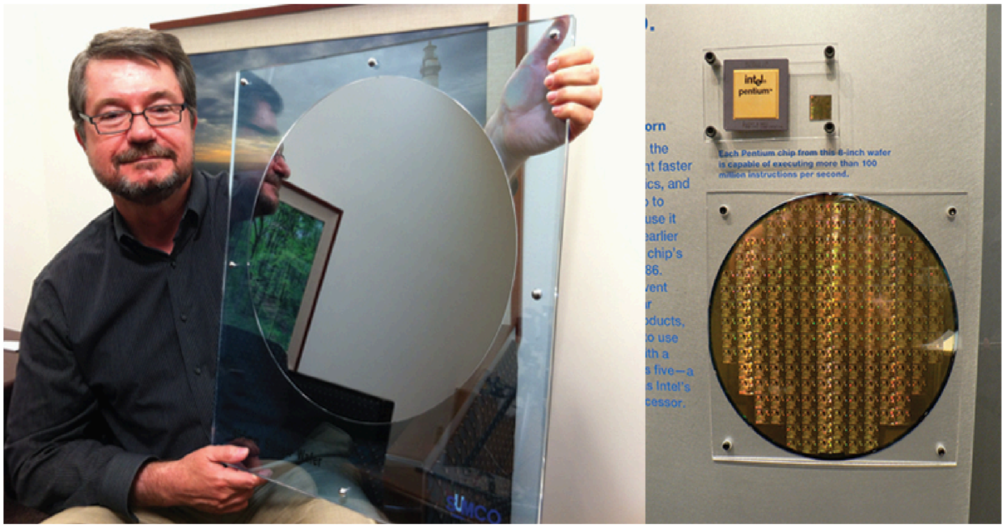

Figure 3a Purity is extremely important when preparing silicon wafers. The CEO of VLSI Research, Don Hutcheson, shows off a pure silicon wafer (left). A silicon wafer covered in Pentium chips is an enlarged version of the silicon wafers found in many electronics used today (right). (credit left: modification of work by Intel Free Press, CC BY 2.0; credit right: modification of work by Naotake Murayama, CC BY 2.0)

The development of the periodic table in the mid-1800s came from observations that there was a periodic relationship between the properties of the elements. Chemists, who have an understanding of the variations of these properties, have been able to use this knowledge to solve a wide variety of technical challenges. For example, silicon and other semiconductors form the backbone of modern electronics because of our ability to fine-tune the electrical properties of these materials. This chapter explores important properties of representative metals, metalloids, and nonmetals in the periodic table.

Attributions & References

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Chemistry (OpenStax) . / Updates for Canadian copyright compliance and student comprehension.

3.1 ELEMENTS

Learning Objectives

By the end of this section, you will be able to:

- Write and interpret symbols that depict the element

Chemical Symbols

A **chemical symbol** is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 3.1a). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).

Figure 3.1a The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. (credit: work by A, PD)

The symbols for several common elements and their atoms are listed in Table 3.1a Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table Figure 3.1c.

Table 3.1a Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists (or occasionally locations); for example, element 106 is now known as *seaborgium* (Sg) in honour of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

Scientists in Action: Marguerite Perey, PhD.

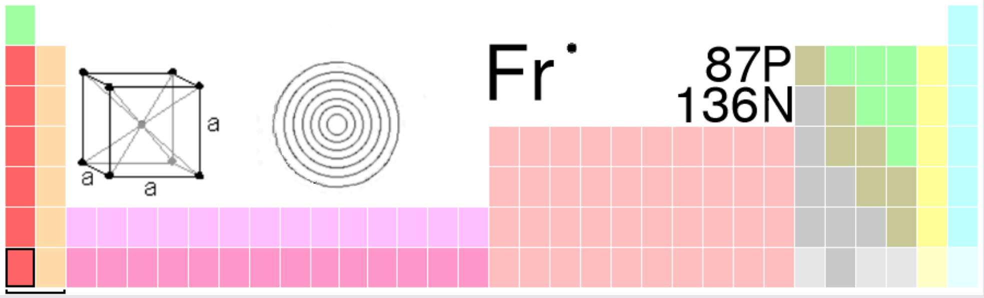
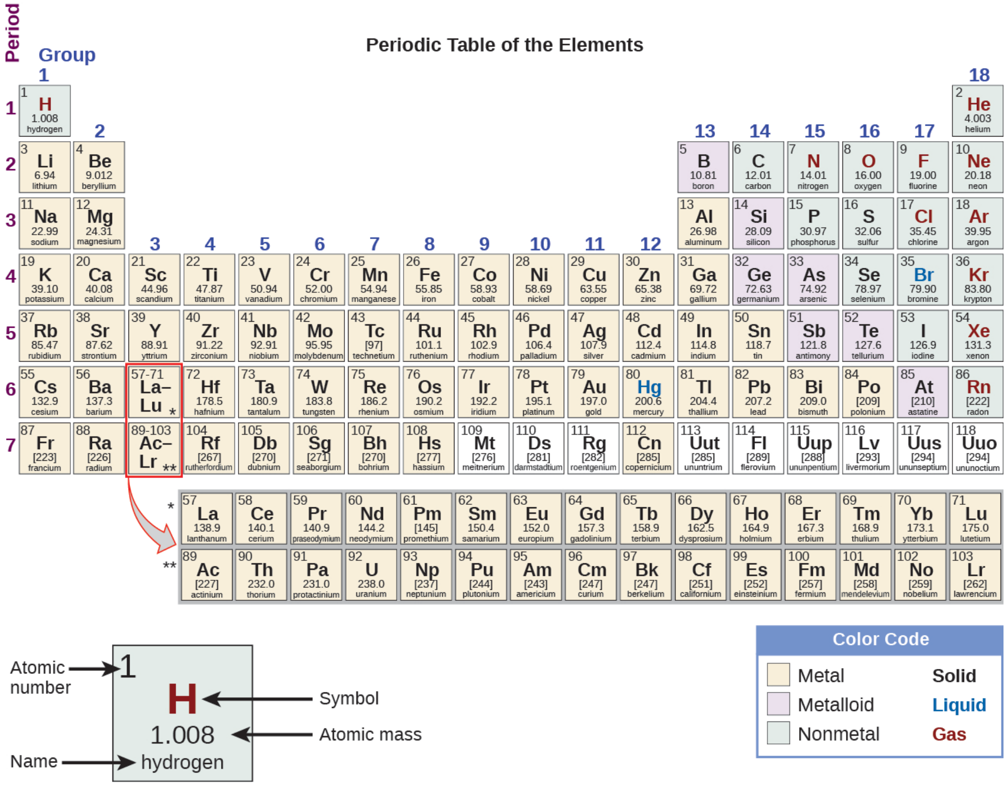


Figure 3.1b Francium (credit: work by Ahoerstemeier, CC BY-SA 3.0)

The discovery of the element 87 on the periodic table is thanks to Marguerite Perey, a French woman scientist. The story of the discovery of element 87, known as Francium, can be found on the Royal Society of Chemistry [New Tab] website. Marguerite Perey was nominated five times for a Nobel Prize but never received one.

Source: Chapman, K. (2020, August 3). Marguerite Perey and the last element in nature. *Chemistry World*. https://www.chemistryworld.com/culture/marguerite-perey-and-the-last-element-in-nature/4012198.article



Periodic Table of the Elements

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008 hydrogen																	2 He 4.003 helium
2	3 Li 6.94 lithium	4 Be 9.012 beryllium											5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La–Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac–Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Uut [285] ununtrium	114 Fl [289] flerovium	115 Uup [288] ununpentium	116 Lv [293] livermorium	117 Uus [294] ununseptium	118 Uuo [294] ununoctium

*	57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
**	89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium

Color Code	
Metal	Solid
Metalloid	Liquid
Nonmetal	Gas

Figure 3.1c Elements and their symbols in the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 3.1a

Check Your Learning Exercise (Text Version)
For each of the following elements listed, write the element's symbol.

a. Magnesium
b. Copper
c. Chlorine
d. Gold
e. Silicon
f. Potassium
g. Iron
h. Tungsten

Check Your Answer[1]

Source: "Exercise 3.1a" by Samantha Sullivan Sauer licensed under CC 4.0.

Links to Interactive Learning Tools

Visit the IUPAC, the International Union of Pure and Applied Chemistry website to learn more about IUPAC, and explore its periodic table.

Practice Name That Element from the Physics Classroom.

Attribution & References

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Notes

1. (a) Mg; (b) Cu; (c) Cl; (d) Au; (e) Si; (f) K; (g) Fe; (h) W;

3.2 THE PERIODIC TABLE

Learning Objectives

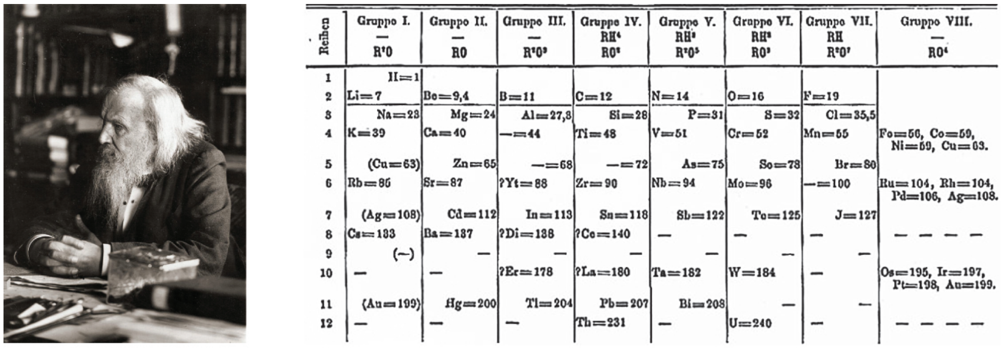
By the end of this section, you will be able to:

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

The Periodic Table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviours. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 3.2a).



Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fo=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	So=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	To=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(a)

(b)

Figure 3.2a (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov, PD; credit b: modification of work by Den fjättrade ankan, PD)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 3.2b). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

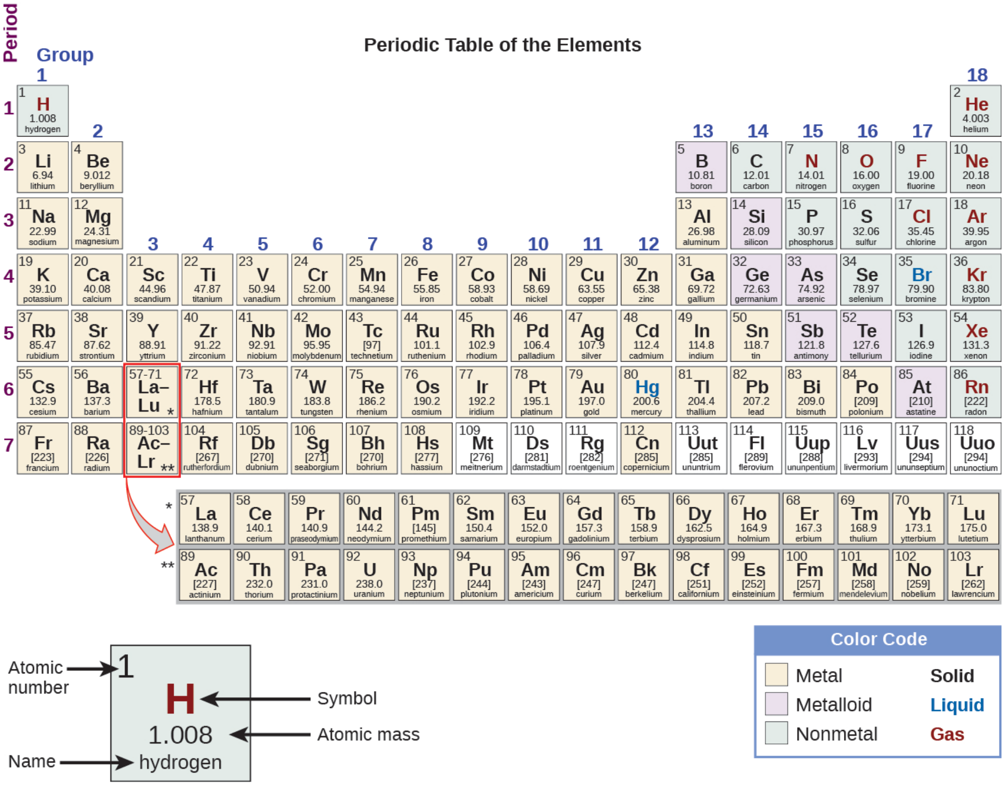


Figure 3.2b Elements in the periodic table are organized according to their properties. Review the [Periodic Table of the Elements in other formats](#) in Appendix A (credit: [*Chemistry (OpenStax)*](#), [CC BY 4.0](#)).

Watch [The Periodic Table Song (2018 Update!) (3:04 mins)](#)

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviours. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); **nonmetals** (elements that appear dull, poor conductors of heat and electricity—shaded green); and **metalloids** (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

Metals

Most of the representative metals do not occur naturally in an uncombined state because they readily react with water and oxygen in the air. However, it is possible to isolate elemental beryllium, magnesium, zinc, cadmium, mercury, aluminum, tin, and lead from their naturally occurring minerals and use them because they react very slowly with air. Part of the reason why these elements react slowly is that these elements react with air to form a protective coating. The formation of this protective coating is **passivation**. The coating is a nonreactive film of oxide or some other compound. Elemental magnesium, aluminum, zinc, and tin are important in the fabrication of many familiar items, including wire, cookware, foil, and many household and personal objects. Although beryllium, cadmium, mercury, and lead are readily available, there are limitations in their use because of their toxicity.

Mercury – An Interesting Metal

Mercury is the only metal that is liquid at 25 °C. Many metals dissolve in mercury, forming solutions called amalgams (see the feature on Amalgams), which are alloys of mercury with one or more other metals. Mercury, shown in Figure 3.2c, is a nonreactive element that is more difficult to oxidize than hydrogen. Thus, it does not displace hydrogen from acids; however, it will react with strong oxidizing acids, such as nitric acid:

$$\mathrm{Hg}(l) + \mathrm{HCl}(aq) \longrightarrow \text{no reaction}$$

$$3\mathrm{Hg}(l) + 8\mathrm{HNO_3}(aq) \longrightarrow 3\mathrm{Hg(NO_3)_2}(aq) + 4\mathrm{H_2O}(l) + 2\mathrm{NO}(g)$$

The clear NO initially formed quickly undergoes further oxidation to the reddish brown NO_2.

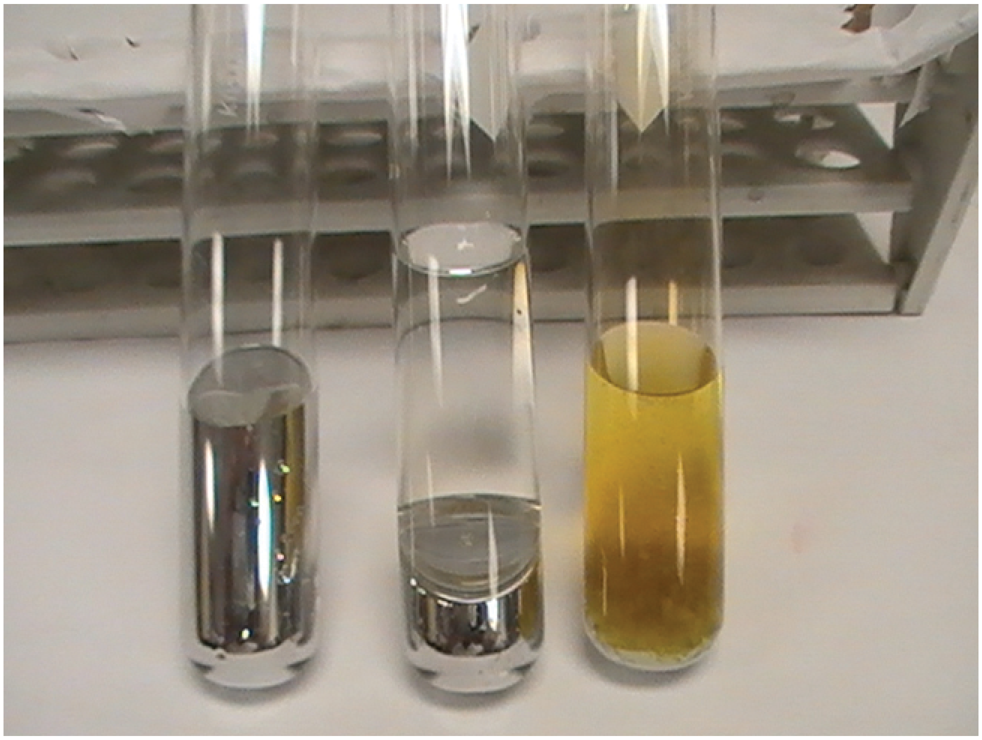


Figure 3.2c From left to right: Hg(*l*), Hg + concentrated HCl, Hg + concentrated HNO_3. (credit: Sahar Atwa in *Chemistry (OpenStax)*, CC BY 4.0).

Amalgams

An amalgam is an alloy of mercury with one or more other metals. This is similar to considering steel to be an alloy of iron with other metals. Most metals will form an amalgam with mercury, with the main exceptions being iron, platinum, tungsten, and tantalum.

Due to toxicity issues with mercury, there has been a significant decrease in the use of amalgams. Historically, amalgams were important in electrolytic cells and in the extraction of gold. Amalgams of the alkali metals still find use because they are strong reducing agents and easier to handle than the pure alkali metals.

Prospectors had a problem when they found finely divided gold. They learned that adding mercury to their pans collected the gold into the mercury to form an amalgam for easier collection. Unfortunately, losses of small amounts of mercury over the years left many streams in California polluted with mercury.

Dentists use amalgams containing silver and other metals to fill cavities. There are several reasons to use an amalgam including low cost, ease of manipulation, and longevity compared to alternate materials. Dental amalgams are approximately 50% mercury by weight, which, in recent years, has become a concern due to the toxicity of mercury.

After reviewing the best available data, the Food and Drug Administration (FDA) considers amalgam-based fillings to be safe for adults and children over six years of age. Even with multiple fillings, the mercury levels in the patients remain far below the lowest levels associated with harm. Clinical studies have found no link between dental amalgams and health problems. Health issues may not be the same in cases of children under six or pregnant women. The FDA conclusions are in line with the opinions of the Environmental Protection Agency (EPA) and Centres for Disease Control (CDC). The only health consideration noted is that some people are allergic to the amalgam or one of its components.

Nonmetals

The nonmetals are elements located in the upper right portion of the periodic table. Their properties and behaviour are quite different from those of metals on the left side. Under normal conditions, more than half of the nonmetals are gases, one is a liquid, and the rest include some of the softest and hardest of solids. The nonmetals exhibit a rich variety of chemical behaviours. They include the most reactive and least reactive of elements, and they form many different ionic and covalent compounds.

Carbon – An Interesting Nonmetal

Carbon occurs in the uncombined (elemental) state in many forms, such as diamond, graphite, charcoal, coke, carbon black, graphene, and fullerene.

Diamond, shown in Figure 3.2d, is a very hard crystalline material that is colourless and transparent when pure. Each atom forms four single bonds to four other atoms at the corners of a tetrahedron (sp^3 hybridization); this makes the diamond a giant molecule. Carbon-carbon single bonds are very strong, and, because they extend throughout the crystal to form a three-dimensional network, the crystals are very hard and have high melting points (~4400 °C).

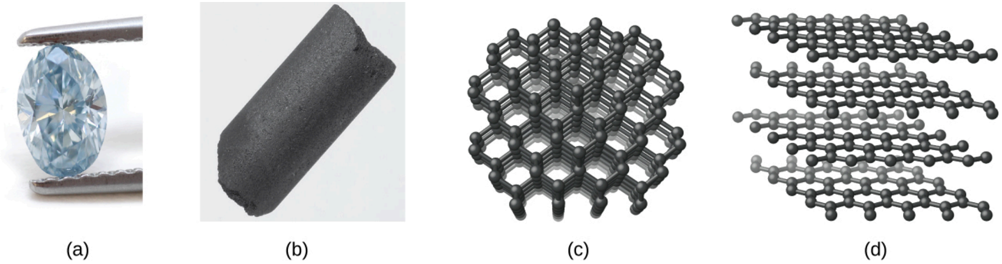


Figure 3.2d (a) Diamond and (b) graphite are two forms of carbon. (c) In the crystal structure of diamond, the covalent bonds form three-dimensional tetrahedrons. (d) In the crystal structure of graphite, each planar layer is composed of six-membered rings. (credit a: modification of work by Fancy Diamonds, CC BY 2.0; credit b: modification of work by Anonymous, CC BY 3.0, credit c, d: *Chemistry (OpenStax)*, CC BY 4.0).

Metalloids

A series of six elements called the metalloids separate the metals from the nonmetals in the periodic table. The metalloids are boron, silicon, germanium, arsenic, antimony, and tellurium. These elements look metallic; however, they do not conduct electricity as well as metals so they are semiconductors. They are semiconductors because their electrons are more tightly bound to their nuclei than are those of metallic conductors. Their chemical behaviour falls between that of metals and nonmetals. For example, the pure metalloids form covalent crystals like the nonmetals, but like the metals, they generally do not form monatomic anions. This intermediate behaviour is in part due to their intermediate electronegativity values.

Boron and Silicon – Two Interesting Metalloids

Boron constitutes less than 0.001% by weight of the earth's crust. In nature, it only occurs in compounds with oxygen. Boron is widely distributed in volcanic regions as boric acid, $B(OH)_3$, and in dry lake regions, including the desert areas of California, as borates and salts of boron oxyacids, such as borax,

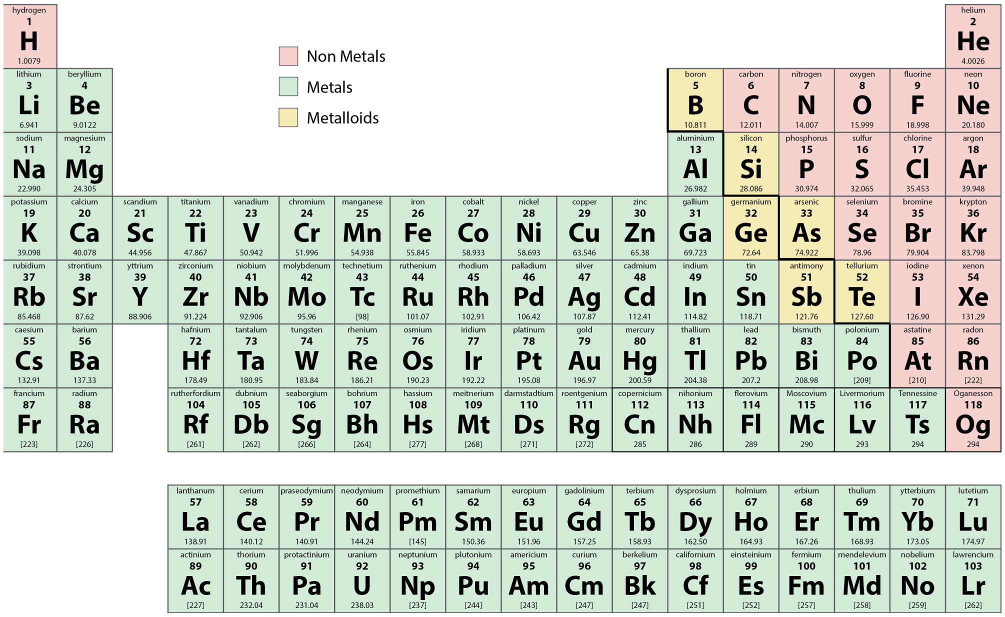
$Na_2B_4O_7{\cdot}10H_2O$. Silicon makes up nearly one-fourth of the mass of the earth's crust—second in abundance only to oxygen. Extremely pure silicon is necessary for the manufacture of semiconductor electronic devices.

Boron burns at 700 °C in oxygen, forming boric oxide, B_2O_3. Boric oxide is necessary for the production of heat-resistant borosilicate glass, like that shown in Figure 3.2e and certain optical glasses. Boric oxide dissolves in hot water to form boric acid, $B(OH)_3$:

$$\mathrm{B_2O_3}(s) \;+\; \mathrm{3H_2O}(l) \longrightarrow \mathrm{2B(OH)_3}(aq)$$

Figure 3.2e Laboratory glassware, such as Pyrex and Kimax, is made of borosilicate glass because it does not break when heated. The inclusion of borates in the glass helps to mediate the effects of thermal expansion and contraction. This reduces the likelihood of thermal shock, which causes silicate glass to crack upon rapid heating or cooling. (credit: photo by Tweenk, CC BY 3.0)

When silicon reacts with oxygen, silicon dioxide is formed. Silicon dioxide, silica, occurs in both crystalline and amorphous forms. The usual crystalline form of silicon dioxide is quartz, a hard, brittle, clear, colourless solid. It is useful in many ways—for architectural decorations, semiprecious jewels, and frequency control in radio transmitters. Silica takes many crystalline forms, or **polymorphs**, in nature. Trace amounts of Fe^{3+} in quartz give amethyst its characteristic purple colour. The term *quartz* is also used for articles such as tubing and lenses that are manufactured from amorphous silica. Opal is a naturally occurring form of amorphous silica.



🟥 Non Metals
🟩 Metals
🟨 Metalloids

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33		hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]		rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [277]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [271]	roentgenium 111 Rg [272]	copernicium 112 Cn 285	nihonium 113 Nh 286	flerovium 114 Fl 289	Moscovium 115 Mc 290	Livermorium 116 Lv 293	Tennessine 117 Ts 294	Oganesson 118 Og 294
			lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05	lutetium 71 Lu 174.97
			actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	lawrencium 103 Lr [262]

Figure 3.2f Metals, non-metals, and metalloids in the periodic table. (credit: graphic by Revathi Mahadevan, CC BY 4.0) Review the Periodic Table of the Elements in other formats in Appendix A.

The Organization of the Periodic Table

The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12; and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**; Figure 3.2f). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and the **noble gases** (group 18, also known as **inert gases**). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1A and group 7A elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

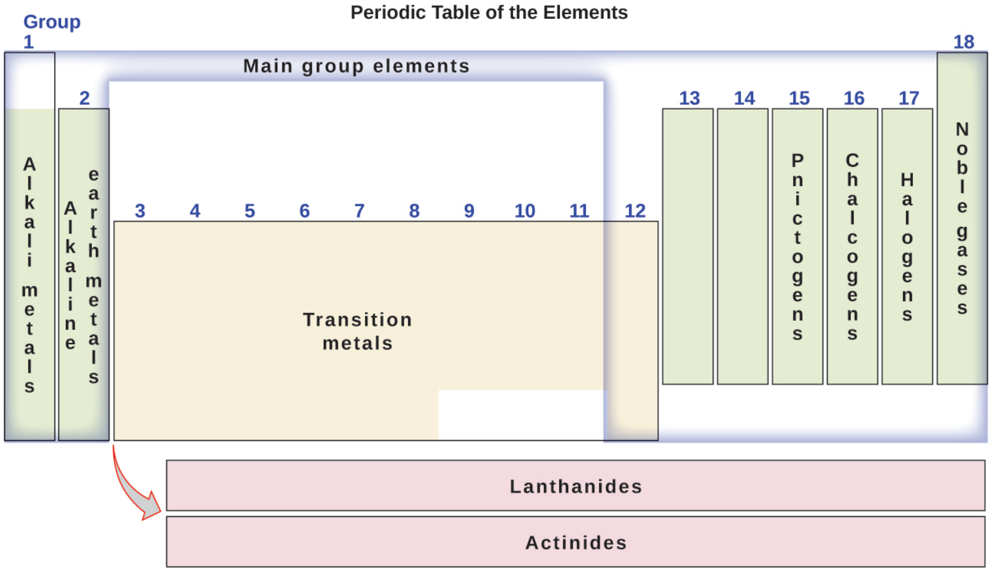


Figure 3.2g The periodic table organizes elements with similar properties into groups. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Group 1: The Alkali Metals

The alkali metals lithium, sodium, potassium, rubidium, cesium, and francium constitute group 1 of the periodic table. Although hydrogen is in group 1, it is a nonmetal. The name alkali metal is in reference to the fact that these metals and their oxides react with water to form very basic (alkaline) solutions.

The properties of the alkali metals are similar to each other as expected for elements in the same family. The alkali metals have the largest atomic radii and the lowest first ionization energy in their periods. This combination makes it very easy to remove the single electron in the outermost (valence) shell of each. The easy loss of this valence electron means that these metals readily form stable cations with a charge of 1+. Their reactivity increases with the increasing atomic number due to the ease of losing the lone valence electron (decreasing ionization energy).

The alkali metals all react vigorously with water to form hydrogen gas and a basic solution of the metal hydroxide.

Group 2: The Alkaline Earth Metals

The **alkaline earth metals** (beryllium, magnesium, calcium, strontium, barium, and radium) constitute group 2 of the periodic table. The name alkaline metal comes from the fact that the oxides of the heavier members of the group react with water to form alkaline solutions. The nuclear charge increases when going from group 1 to group 2. Because of this charge increase, the atoms of the alkaline earth metals are smaller and have higher first ionization energies than the alkali metals within the same period. The higher ionization energy makes the alkaline earth metals less reactive than the alkali metals; however, they are still very reactive elements. Their reactivity increases, as expected, with increasing size and decreasing ionization energy. In chemical reactions, these metals readily lose both valence electrons to form compounds in which they exhibit an oxidation state of 2+.

Groups 7 and 8: Halogens and Noble Gases

The noble gases are all monatomic, whereas the other nonmetal gases—hydrogen, nitrogen, oxygen, fluorine, and chlorine—normally exist as the diatomic molecules H_2, N_2, O_2, F_2, and Cl_2. The other halogens are also diatomic; Br_2 is a liquid and I_2 exists as a solid under normal conditions.

Halogens

Halogens are found in group 17 (or 7A) within the periodic table. These include Fluorine, Chlorine, Bromine and Iodine. Fluorine is a pale yellow gas, chlorine is a greenish-yellow gas, bromine is a deep reddish-brown liquid, and iodine is a grayish-black crystalline solid. Liquid bromine has a high vapour pressure, and the reddish vapour is readily visible in Figure 3.2g. Iodine crystals have a noticeable vapour pressure. When gently heated, these crystals sublime and form a beautiful deep violet vapour.

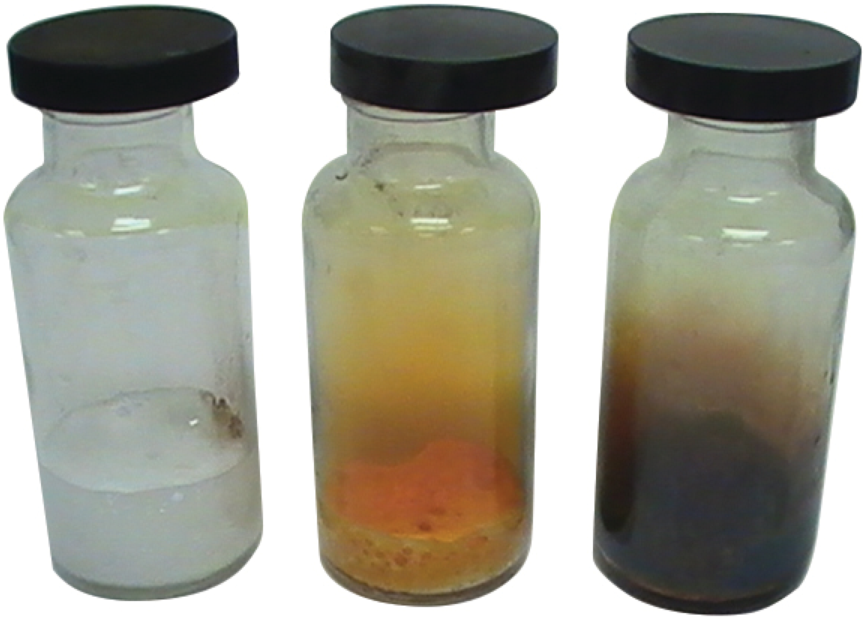


Figure 3.2h Chlorine is a pale yellow-green gas (left), gaseous bromine is deep orange (centre), and gaseous iodine is purple (right). (Fluorine is so reactive that it is too dangerous to handle.) (credit: Sahar Atwa in *Chemistry (OpenStax)*, CC BY 4.0).

The Noble Gases

The elements in group 18 (or 8A) are the noble gases (helium, neon, argon, krypton, xenon, and radon). They earned the name "noble" because they were assumed to be nonreactive since they filled valence shells. In 1962, Dr. Neil Bartlett at the University of British Columbia proved this assumption to be false.

These elements are present in the atmosphere in small amounts. Some natural gas contains 1–2% helium by mass. Helium is isolated from natural gas by liquefying the condensable components, leaving only helium as a gas. The United States possesses most of the world's commercial supply of this element in its helium-bearing gas fields. Argon, neon, krypton, and xenon come from the fractional distillation of liquid air. Radon comes from other radioactive elements. More recently, it was observed that this radioactive gas is present in very small amounts in soils and minerals. Its accumulation in well-insulated, tightly sealed buildings, however, constitutes a health hazard, primarily lung cancer.

Exercise 3.2a

Check Your Learning Exercise (Text Version)

Atoms of elements are essential for life. Identify the group name (Alkali Metal, Gas, **Chalcogen**, Alkaline Earth Metal, Halogen) that each of the following elements belong to:

a. chlorine belongs to
b. calcium and barium belongs to
c. sodium and lithium belongs to
d. sulfur and selenium belongs to
e. krypton belongs to

Check Your Answer[1]

Source: "Exercise 3.1a" is adapted from "3.6 The Periodic Table Example 1" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

Links to Interactive Learning Tools

Click on the interactive periodic table, from the Royal Society of Chemistry, which you can use to explore the properties of the elements (includes podcasts and videos of each element).

Classify Metals, Metalloids and Nonmetals from the Physics Classroom.

Explore the Classification of Matter from the Physics Classroom.

Explore Elements, Atoms, and Ions Practice from eCampusOntario H5P Studio.

Make a New Periodic Table from eCampusOntario H5P Studio.

Attribution & References

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Notes

1. (a) Halogen; (b) Alkaline Earth Metal; (c) Alkali Metal; (d) Chalcogen; (e) Gas

3.3 COMPOUNDS AND FORMULAS

Learning Objectives

By the end of this section, you will be able to:

- Define molecular and structural formulas
- Define ionic and molecular (covalent) compounds
- Determine the number of atoms of each element in a compound

Chemical Formulae

A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The **structural formula** for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure 3.3a). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For structural formula now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

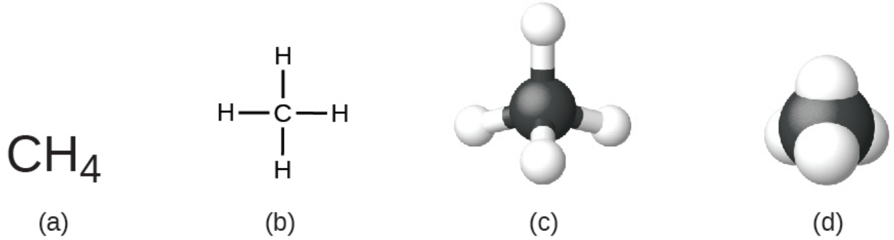

Figure 3.3a A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called **diatomic molecules**) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 3.3b).

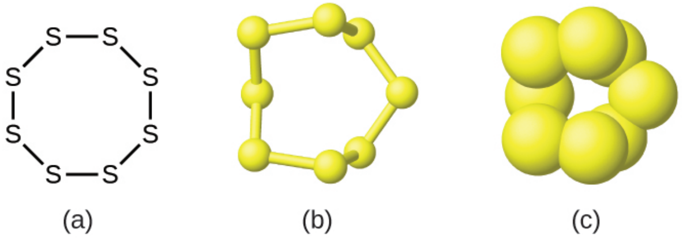

Figure 3.3b A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres (credit: *Chemistry (OpenStax)*, CC BY 4.0).

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 3.3c.).

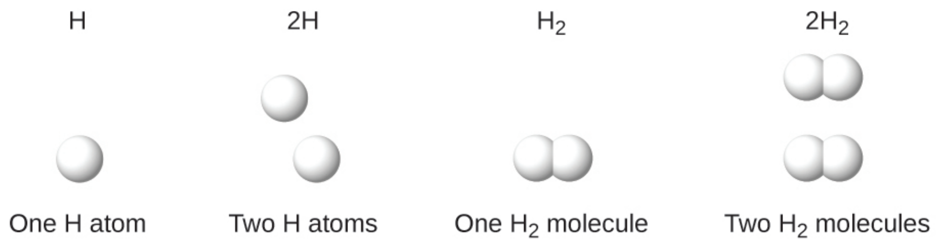

Figure 3.3c The symbols H, 2H, H_2, and $2H_2$ represent very different entities (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt.

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure 3.3d).

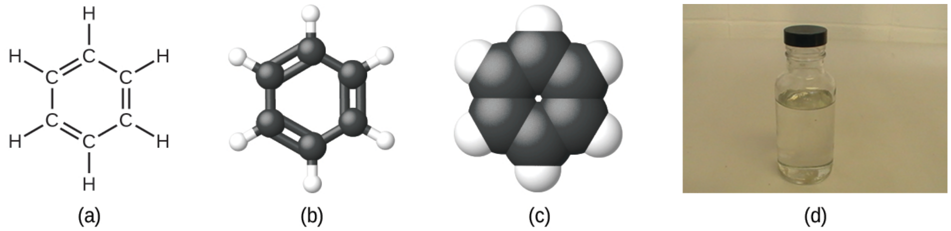

Figure 3.3d Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa in *Chemistry (OpenStax)*, CC BY 4.0)

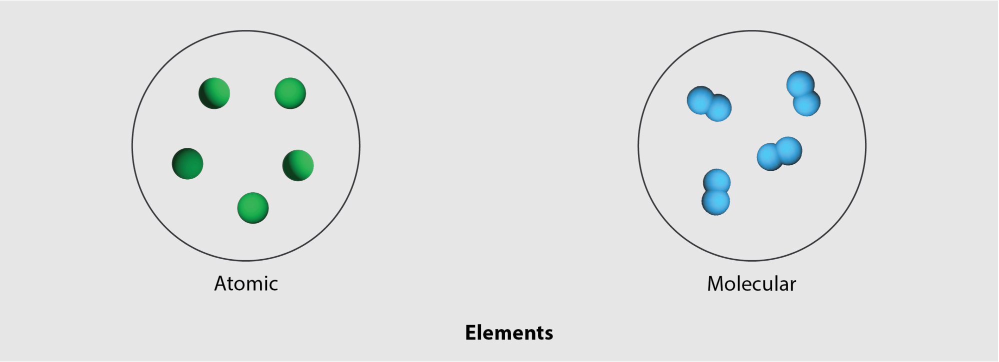

Figure 3.3e The figure illustrates the difference in the atomic structure of an element. (credit: modification of work by Hoa112008, PD; / Adapted by Revathi Mahadevan, CC BY 4.0).

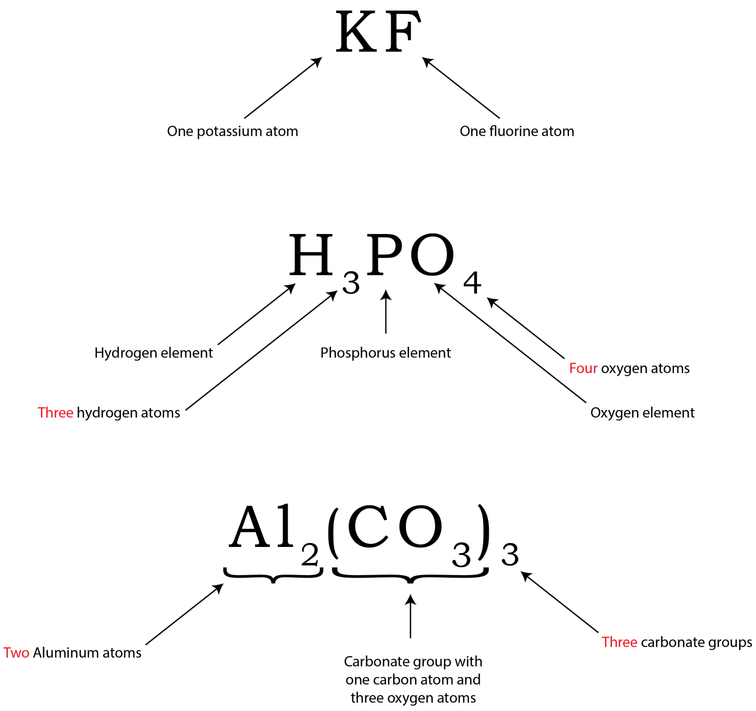

Figure 3.3f Breakdown of compounds. (credit: graphic by Revathi Mahadevan, CC BY 4.0)

Example 3.3a

Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What is the molecular formula of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms.

Exercise 3.3a

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What is the molecular formula of metaldehyde?

Check Your Answer[1]

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures.

Example 3.3b

Determine the number of atoms of each element and the total number of atoms for the compound $AlCl_3$?

Solution

1 Al atom

3 Cl atoms

Total number of atoms in $AlCl_3$ is 4 atoms since 1 Al atom + 3 Cl atoms = 4 total atoms

Source: "Example 3.3b" by Adrienne Richards is licensed under CC BY NC 4.0.

Example 3.3c

How many atoms of each element and the total number of atoms are present in the compound $CaCO_3$?

Answer

1 Ca

1 C

3 O

The total number of atoms in $CaCO_3$ is 5 since 1 Ca + 1 C + 3 O = 5 atoms.

Source: “Example 3.3c” by Adrienne Richards is licensed under CC BY NC 4.0.

The Formation of Chemical Compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called **ions** (Figure 3.3e).

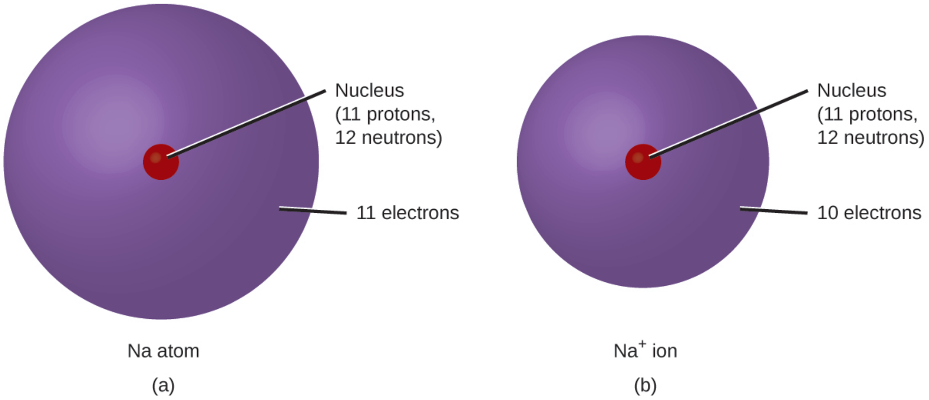

Figure 3.3g (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, **cations** and **anions**). When electrons are “shared” and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

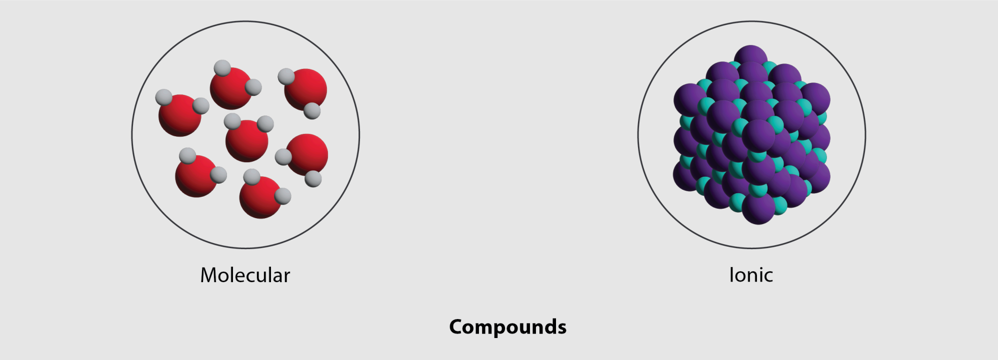

Figure 3.3h The figure illustrates the difference in atomic structure in a compound. (credit: graphic by Revathi Mahadevan, CC BY 4.0)

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic.

Watch Conductivity molten salt (1 mins)

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These **molecular compounds** (**covalent compounds**) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals.

Scientists in Action: Dr. Uma Chowdhry

Figure 3.3i Dr. Uma Chowdhry (credit: Photo by Science History Institute, CC BY-SA 3.0)

Dr. Uma Chowdhry is a retired senior vice president and chief science and technology officer for DuPont, where she worked from 1977 to 2010. She was born in Mumbai, then came to the U.S. for her Masters Degree from Caltech and her PhD in material science from MIT.

Dr. Chowdhry started as a research scientist for Dupont and, throughout her career, she was responsible for overseeing a large number of projects. In 1987 the research efforts she led in ceramic superconducting materials generated over 20 patents and 50 publications.

There is a very good chance you own something that relies on materials and technology developed by DuPont during Dr. Chowdhry's time.

See Dr. Chowdhry talking more about her life in Women in Chemistry: Uma Chowdhry [New Tab].

Links to Interactive Learning Tools

Practice Chemical Formulas and Atom Counting by the Physics Classroom.

Attribution & References

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- "2.6 Ionic and Molecular Compounds" In *Chemistry 2e (OpenStax)* by Paul Flowers, Klaus Theopold,

Notes

1. Molecular formula, $C_8H_{16}O_4$

CHAPTER 3 SUMMARY

3.1 Elements

A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms. The chemical symbols represent the element found on the periodic table.

3.2 The Periodic Table

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. This means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

3.3 Compounds and Formulas

Compounds that contain ions are called ionic compounds. Ionic compounds generally form between metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. A structural formula indicates the bonding arrangement of the atoms in the molecule.

Attribution & References

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CHAPTER 3 REVIEW

3.1 Elements; and 3.2 The Periodic Table

1. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:
   a. uranium
   b. bromine
   c. strontium
   d. neon
   e. gold
   f. americium
   g. rhodium
   h. sulfur
   i. carbon
   j. potassium
   Check answers: [1]
2. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:
   a. cobalt
   b. europium
   c. iodine
   d. indium
   e. lithium
   f. oxygen
   g. cadmium
   h. terbium
   i. rhenium
3. Using the periodic table, identify the lightest member of each of the following groups:
   a. noble gases
   b. alkaline earth metals
   c. alkali metals

   d. chalcogens

      Check answers: [2]

4. Using the periodic table, identify the heaviest member of each of the following groups:
   a. alkali metals
   b. chalcogens
   c. noble gases
   d. alkaline earth metals
5. Use the periodic table to give the name and symbol for each of the following elements:
   a. the noble gas in the same period as germanium
   b. the alkaline earth metal in the same period as selenium
   c. the halogen in the same period as lithium
   d. the chalcogen in the same period as cadmium

      Check answers: [3]

3.3 Compounds and Formulas

1. Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

   Check answers: [4]
2. Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.
3. For each of the following compounds, state whether it is ionic or covalent; write the number of atoms of each element in the compound and the total number of atoms present.
   a. NF_3
   b. BaO
   c. $(NH_4)_2CO_3$
   d. $Sr(H_2PO_4)_2$
   e. IBr
   f. Na_2O

      Check answers: [5]
4. For each of the following compounds, state whether it is ionic or covalent; write the number of atoms of each element in the compound and the total number of atoms present.
   a. $KClO_4$
   b. $MgC_2H_3O_2$
   c. H_2S
   d. Ag_2S
   e. N_2Cl_4

   f. $Co(NO_3)_2$
5. For each of the following pairs of ions, write the symbol for the formula of the compound they will form:
   a. Ca^{2+}, S^{2-}
   b. NH_4^+, SO_4^{2-}
   c. Al^{3+}, Br^-
   d. Na^+, HPO_4^{2-}
   e. Mg^{2+}, PO_4^{3-}
   Check answers:[6]
6. For each of the following pairs of ions, write the symbol for the formula of the compound they will form:
   a. K^+, O^{2-}
   b. NH_4^+, PO_4^{3-}
   c. Al^{3+}, O^{2-}
   d. Na^+, CO_3^{2-}
   e. Ba^{2+}, PO_4^{3-}

Attribution & References

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Notes

1. (a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative
2. (a) He; (b) Be; (c) Li; (d) O
3. (a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te
4. 1. Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4
5. (a) covalent; 1 Na, 3F, Total 4 atoms (b) ionic; 1 Ba, 1 O, Total 3 atoms (c) ionic; 2 N, 8H, 1 C, 3 O, Total 14 atoms (d) ionic; 1 Sr, 4 H, 2 P, 8 O, Total 15 atoms (e) covalent; 1 I, 1 Br, Total 2 atoms (f) ionic; 2 Na, 1 O, Total 3 atoms.
6. (a) CaS; (b) $(NH_4)_2SO_4$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3(PO_4)_2$

CHAPTER 4. MATTER AND ITS PROPERTIES

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The linkages between chemical and physical properties
- Quantifying energy contained within chemical bonds and reactions

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- The periodic table

Figure 4a Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: work by Laszlo Ilyes, CC BY 2.0)

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[1] While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

Scientists in Action: Dr. Constantine Alberga Campbell

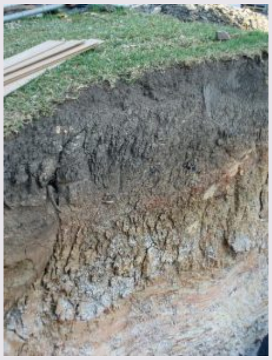

Figure 4b Soil profile (credit: work by Science StockPhotos, CC BY 4.0)

Born in Jamaica, Dr. Constantine Alberga Campbell is one of the leading soil scientists in Canada. His research centered on agricultural dryland soils and led to more productive, profitable and sustainable farming. His findings were presented in manner that allowed industry and producers to understand and apply the knowledge. Dr. Campbell was among the first to radiocarbon date soil organic matter. His published work in 1967 is cited as a landmark work. Read more about Constantine Alberga Campbell [New Tab].

Source: *Constantine Alberga Campbell*. (2010, December 15). Science.ca.

Attributions & References

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Notes

1. US Energy Information Administration, *Primary Energy Consumption by Source and Sector, 2012*, http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css_2012_energy.pdf. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

4.1 PHYSICAL AND CHEMICAL PROPERTIES

Learning Objectives

By the end of this section, you will be able to:

- Identify properties of and changes in matter as physical or chemical
- Distinguish between physical and chemical properties
- Identify properties of matter as extensive or intensive

The characteristics that enable us to distinguish one substance from another are called properties. A **physical property** is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, colour, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and colour, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change.

A **physical change** is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure 4.1a). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in colour). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.


(a) (b)

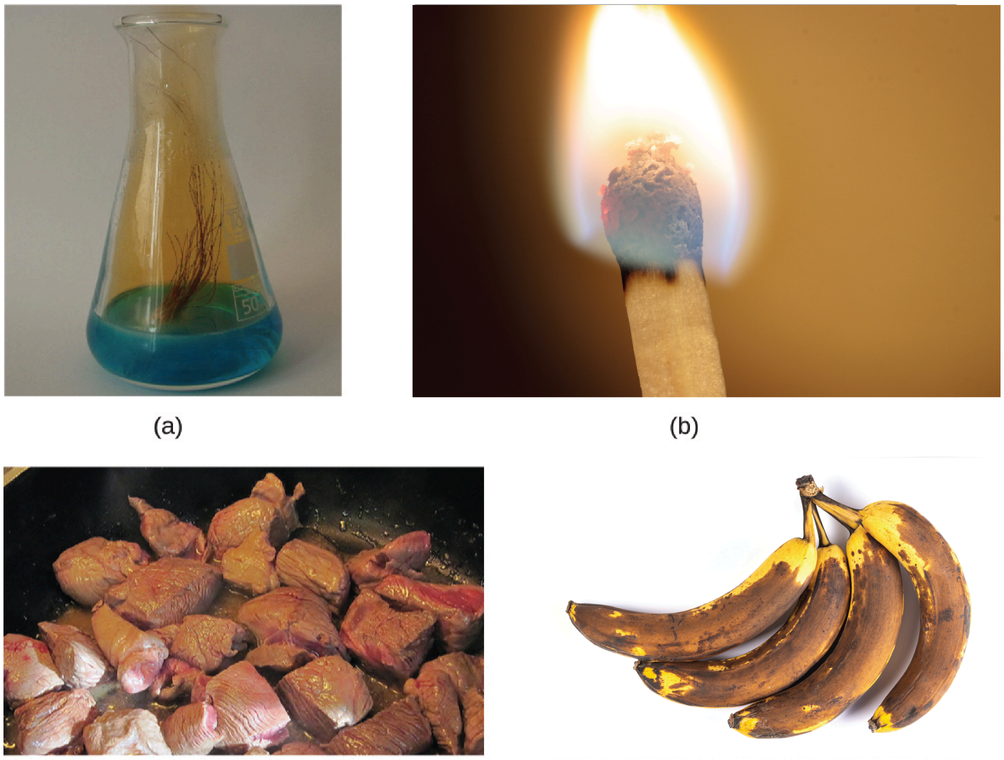
Figure 4.1a (a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapour is changed into liquid water. (credit a: modification of work by 95jb14, PD; credit b: modification of work by mjneuby, CC BY 2.0)

The change of one type of matter into another type (or the inability to change) is a **chemical property**. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure 4.1b). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.


(a) (b)

Figure 4.1b (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett, CC BY 2.0; credit b: modification of work by Atoma, CC BY 2.5)

To identify a chemical property, we look for a chemical change. A **chemical change** always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure 4.1c).



(a) (b)

(c) (d)

Figure 4.1c (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapour. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown colour change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit a: work by The mad scientist, PD; credit b: work by Francesco Schiavone, CC BY 4.0; credit c: modification of work by Gloria Cabada-Leman, CC BY 2.0; credit d: work by Marco Verch, CC BY 2.0)

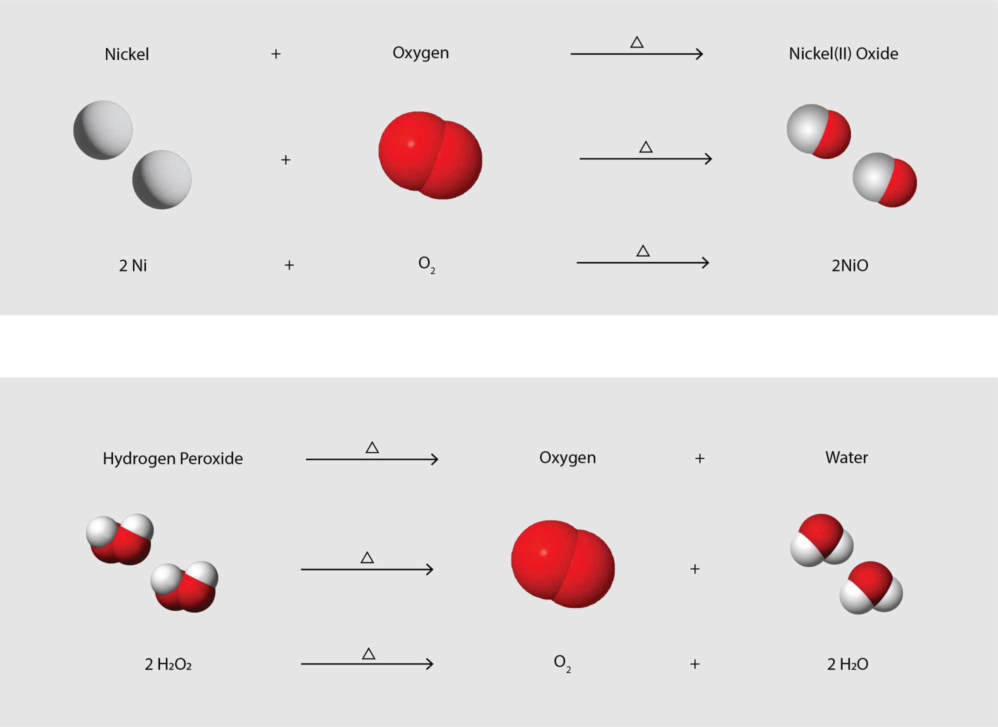


Figure 4.1d The figure illustrates the example of chemical changes undergone to form Nickel(II) Oxide and the decomposition of hydrogen peroxide. (credits: modification of oxygen by Ulflund, CC0; hydrogen peroxide by Benjah-bmm27, PD; water by Dbc334 & Jynto (Water), PD / Combined/Adapted by Revathi Mahadevan, CC BY 4.0)

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an **extensive property**. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass and volume than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an **intensive property**. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

Hazard Diamond

You may have seen the symbol shown in Figure 4.1d on containers of chemicals in a laboratory or workplace. Sometimes called a “fire diamond” or “hazard diamond,” this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.

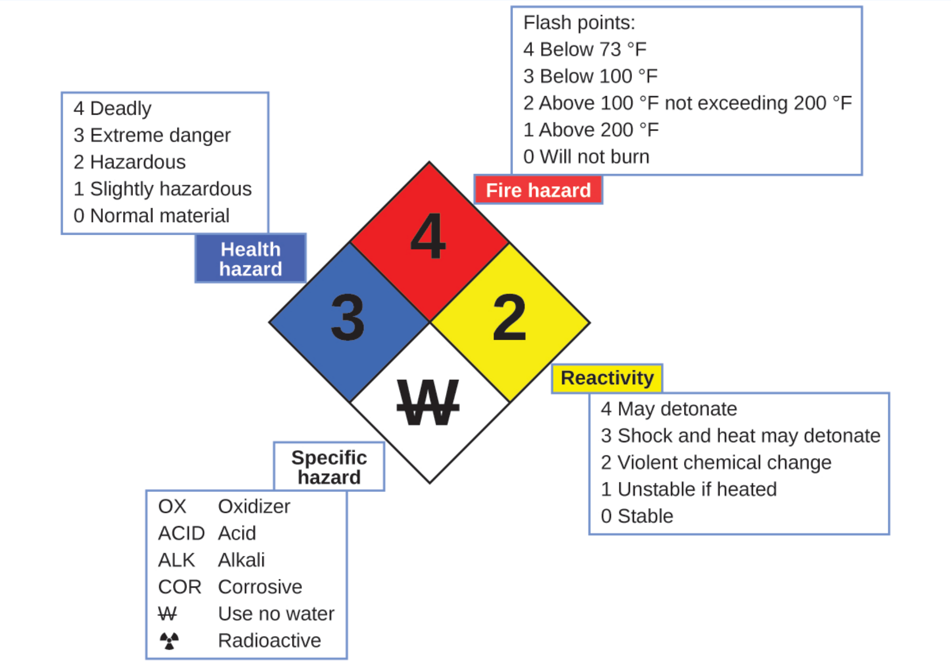
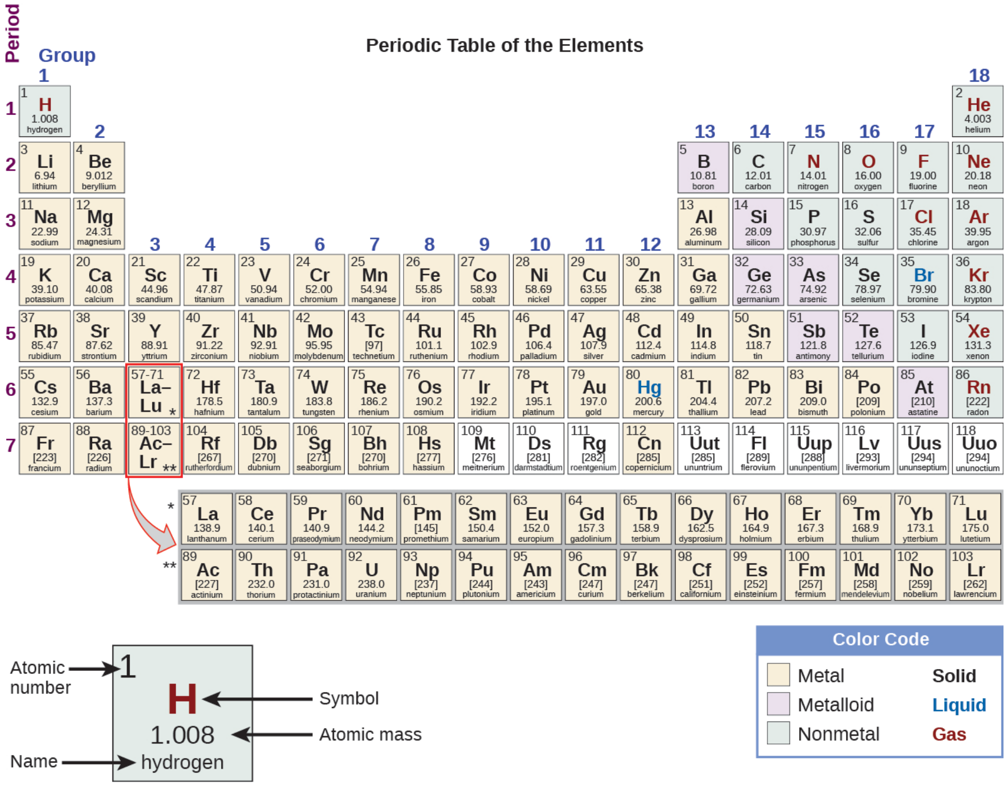


Figure 4.1e The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The National Fire Protection Agency (NFPA) 704 Hazard Identification System was developed by NFPA to provide safety information about certain substances. The system details flammability, reactivity, health, and other hazards. Within the overall diamond symbol, the top (red) diamond specifies the level of fire hazard (temperature range for flash point). The blue (left) diamond indicates the level of health hazard. The yellow (right) diamond describes reactivity hazards, such as how readily the substance will undergo detonation or a violent chemical change. The white (bottom) diamond points out special hazards, such as if it is an oxidizer (which allows the substance to burn in the absence of air/oxygen), undergoes an unusual or dangerous reaction with water, is corrosive, acidic, alkaline, a biological hazard, radioactive, and so on. Each hazard is rated on a scale from 0 to 4, with 0 being no hazard and 4 being extremely hazardous.

While many elements differ dramatically in their chemical and physical properties, some elements have similar properties. We can identify sets of elements that exhibit common behaviours. For example, many elements conduct heat and electricity well, whereas others are poor conductors. These properties can be used to sort the elements into three classes: metals (elements that conduct well), nonmetals (elements that conduct poorly), and metalloids (elements that have properties of both metals and nonmetals).

The periodic table is a table of elements that places elements with similar properties close together (Figure 4.1f). You will learn more about the periodic table as you continue your study of chemistry.



Periodic Table of the Elements

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008 hydrogen																	2 He 4.003 helium
2	3 Li 6.94 lithium	4 Be 9.012 beryllium											5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La–Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac–Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Uut [285] ununtrium	114 Fl [289] flerovium	115 Uup [288] ununpentium	116 Lv [293] livermorium	117 Uus [294] ununseptium	118 Uuo [294] ununoctium

*	57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
**	89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium

Color Code	
Metal	Solid
Metalloid	Liquid
Nonmetal	Gas

Figure 4.1f The periodic table shows how elements may be grouped according to certain similar properties. Note the background colour denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol colour indicates whether it is a solid, liquid, or gas. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 4.1a

Check Your Learning Exercise (Text Version)
Classify each of the following descriptions as either a physical or chemical property.

a. acid is corrosive to the skin
b. the ice will melt at 10 degrees Celsius
c. the sunburn is red
d. hydrochloric acid is very acidic
e. a person’s hair is brown
f. arsenic is very poisonous

g. insecticides kill insects
h. water boils at 100 degrees Celsius
i. the ice is cold
j. the glass is not flammable
k. helium gas is nonreactive
l. the cake is very dense

Check Your Answer[1]

Source: "Exercise 4.1a" created by Jackie MacDonald, CC BY-NC-SA-4.0.

Exercise 4.1b

Check Your Learning Exercise (Text Version)
Classify each of the following as either a physical or chemical change:

a. Condensation of steam
b. Burning of gasoline
c. Souring of milk
d. Melting of gold

Check Your Answer[2]

Source: "Exercise 4.1b" is adapted from "Exercise 1.3-2" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Links to Interactive Learning Tools

Explore Chemical Vs. Physical Properties from the Physics Classroom.

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Notes

1. (a) chemical; (b) physical; (c) physical; (d) chemical; (e) physical; (f) chemical; (g) chemical; (h) physical; (i) physical; (j) chemical; (k) chemical; (l) physical
2. (a) Physical; (b) Chemical; (c) Chemical; (d) Physical;

4.2 ENERGY BASICS

Learning Objectives

By the end of this section, you will be able to:

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure 4.2a). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.


(a) (b) (c)

Figure 4.2a The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by D Sharon Pruitt, CC BY 2.0; credit b: modification of work by Jeffery Turner, CC BY 2.0; credit c: work by Unknown, PD.)

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products. An example of this such a product is ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavour to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of **work (*w*)** is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 4.2b). A battery has potential energy because the chemicals within it can produce electricity that can do work.

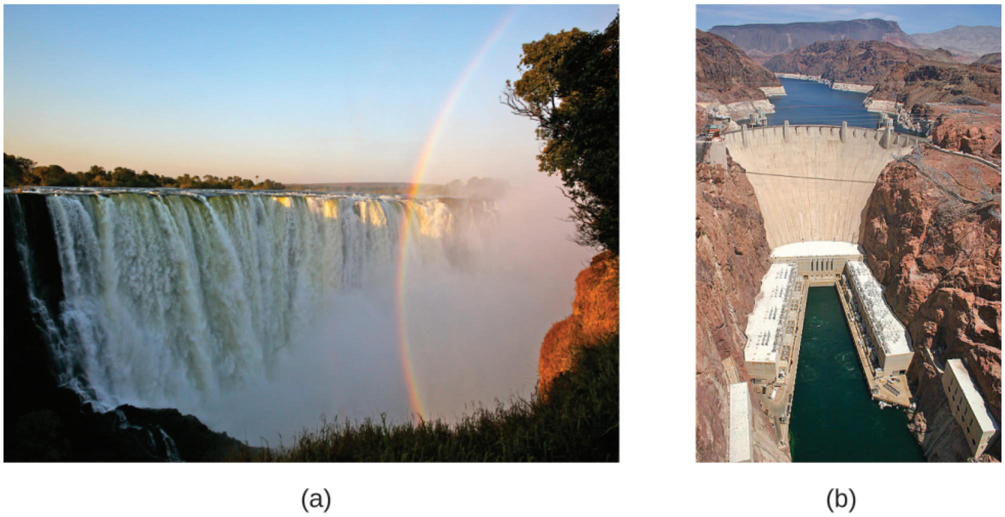

Figure 4.2b (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam showed here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson, CC BY 2.0; credit b: modification of work by curimedia, CC BY 2.0)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

Thermal energy is the kinetic energy associated with the random motion of atoms and molecules. **Temperature** is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure 4.2c). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

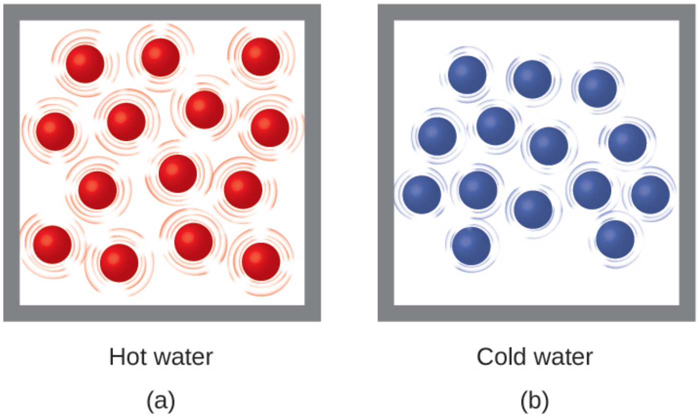

Figure 4.2c (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 4.2a

Practice using the following PhET simulation: States of Matter

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 4.2d. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

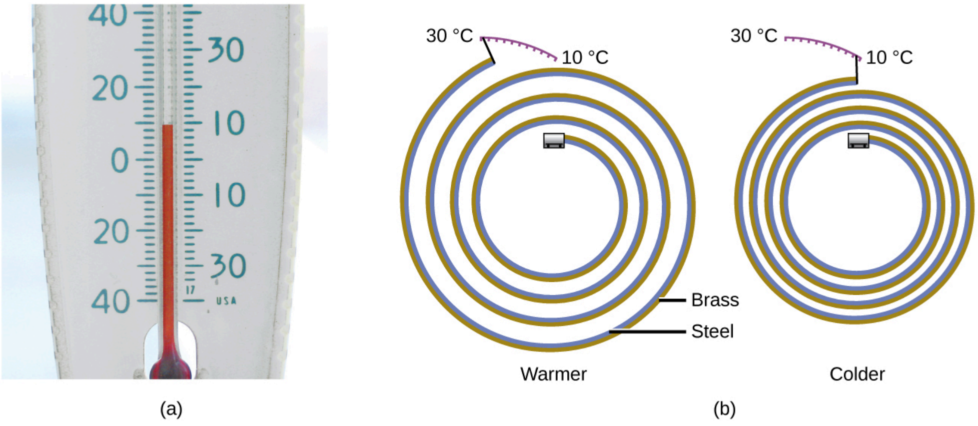

Figure 4.2d (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by dwstucke, CC BY 2.0, credit b: *Chemistry (OpenStax)*, CC BY 4.0).

Watch How does a bimetallic strip thermometer work? (4 mins)

Heat (*q*) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high-temperature (and high thermal energy) substance (H) and a low-temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 4.2e).

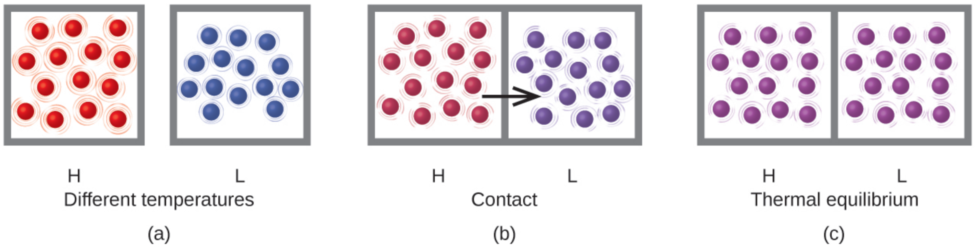

Figure 4.2e (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 4.2b

Practice using the following PhET simulation: Energy Forms and Changes

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 4.2f). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

(a) (b)

Figure 4.2f (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by Skatebiker, PD; credit b: *Chemistry (OpenStax)*, CC BY 4.0).

Historically, energy was measured in units of **calories (cal)**. A calorie is the amount of energy required to raise one gram of water by 1 degree C. However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A **joule (J)** is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is joule (J) named in honour of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity (*C*)** of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

$$C_{\text{small pan}} = \frac{18,140\ \text{J}}{50.0\ {}^\circ\text{C}} = 363\ \text{J}/{}^\circ\text{C}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700\ \text{J}}{50.0\ {}^\circ\text{C}} = 1814\ \text{J}/{}^\circ\text{C}$$

The **specific heat capacity (*c*)** of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$C = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is, therefore:

$$c_{\text{iron}} = \frac{18,140\ \text{J}}{(808\ \text{g})(50.0\ {}^\circ\text{C})} = 0.449\ \text{J/g}\ {}^\circ\text{C}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700\ \text{J}}{(4040\ \text{g})(50.0\ {}^\circ\text{C})} = 0.449\ \text{J/g}\ {}^\circ\text{C}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). (Figure 4.2g).

Figure 4.2g Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser in *Chemistry (OpenStax)*, CC BY 4.0).

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 4.2a.

Table 4.2a Specific Heats of Common Substances at 25 °C and 1 bar

Substance	**Symbol (*state*)**	**Specific Heat (J/g °C)**
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapour	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$\begin{aligned} q = &\quad \text{(specific heat)} \times \text{(mass of substance)} \times \text{(temperature change)} \\ q = &\quad c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned}$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read "delta T") is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example 4.2a

Measuring Heat

A flask containing 8.0 × 10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned} \boldsymbol{q} \quad &= \boldsymbol{c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})} \\ &= \mathbf{(4.184\ J/\cancel{g}\ {}^{\circ}C \times (800\ \cancel{g}) \times (85 - 20)\ {}^{\circ}C} \\ &= \mathbf{(4.184\ J/\cancel{g}\ {}^{\circ}\cancel{C} \times (800\ \cancel{g}) \times (625)\ {}^{\circ}\cancel{C}} \\ &= \mathbf{210,000\ J(= 210\ kJ)} \end{aligned}$$

Because the temperature increased, the water absorbed heat and *q* is positive.

Exercise 4.2c

How much heat, in joules, must be added to a 5.00 × 10^2-g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Check Your Answer[1]

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Exercise 4.2d

Check Your Learning Exercise (Text Version)
How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from −23.0 °C to −1.0 °C?

Check Your Answer[2]

Source: "Exercise 4.2d" is adapted from "Exercise 9.1-7" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 4.2b

Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

$$6640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) \ ^\circ\text{C}$$

Solving:

$$c = \frac{6640 \text{ J}}{(348 \text{ g}) \times (21.2 \ ^\circ\text{C})} = 0.900 \text{ J/g} \ ^\circ\text{C}$$

Comparing this value with the values in Table 4.2a, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 4.2e

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Check Your Answer[3]

Exercise 4.2f

Check Your Learning Exercise (Text Version)
Calculate the heat capacity, in joules and in calories per degree, of the following:

a. 45.8 g of nitrogen gas
b. 1.00 pounds of aluminum metal

Check Your Answer[4]

Source: "Exercise 4.2f" is adapted from "Exercise 9.1-5" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 4.2h). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

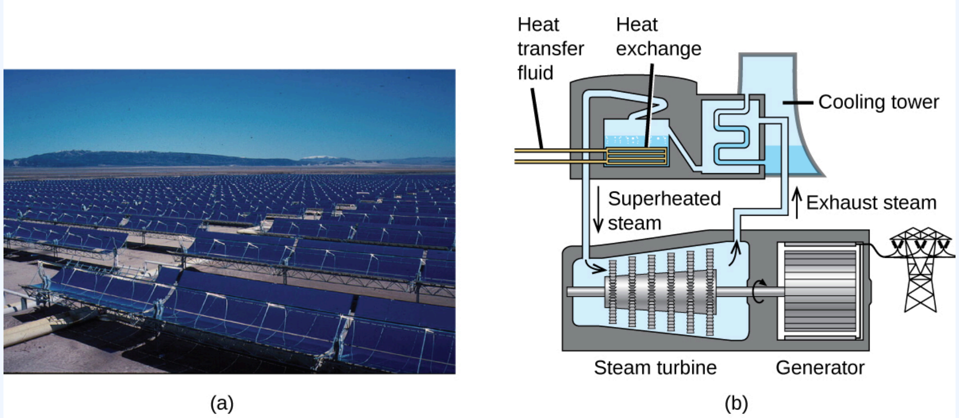

Figure 4.2h This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management, PD; credit b: *Chemistry (OpenStax)*, CC BY 4.0).)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 4.2i). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.

Figure 4.2i (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich, CC BY 2.0; credit b: modification of work by USFWS Pacific Southwest Region, CC BY 2.0)

Links to Interactive Learning Tools

Explore Measuring the Quantity of Heat from the Physics Classroom.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Attribution & References

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Notes

1. 5.05×10^4 J
2. 1310 J and 313 cal
3. c = 0.45 J/g °C; the metal is likely to be iron
4. (a) 47.6 J per degree celsius; 11.38 cal per degree celsius; (b) 97.3 cal per degree celsius; 407 J per degree celsius

4.3 CALORIMETRY

Learning Objectives

By the end of this section, you will be able to:

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as **calorimetry**. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a **system** (the substance or substances undergoing the chemical or physical change) and its **surroundings** (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in a solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 4.3a). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

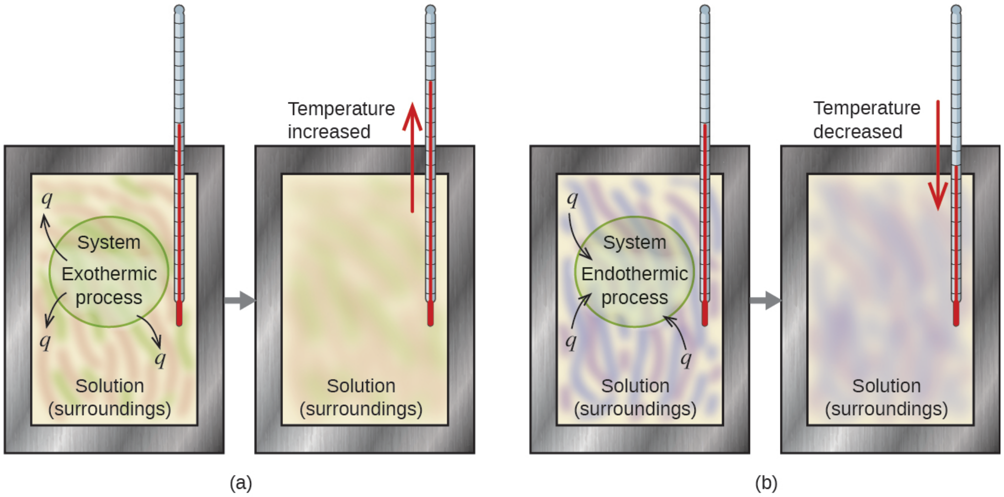


Figure 4.3a In a calorimetric determination, either (a) an exothermic process occurs and heat, *q*, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, *q*, is positive, indicating that thermal energy is transferred from the surroundings to the system (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure 4.3b). These easy-to-use "coffee cup" calorimeters allow more heat exchange with their surroundings and therefore produce less accurate energy values.

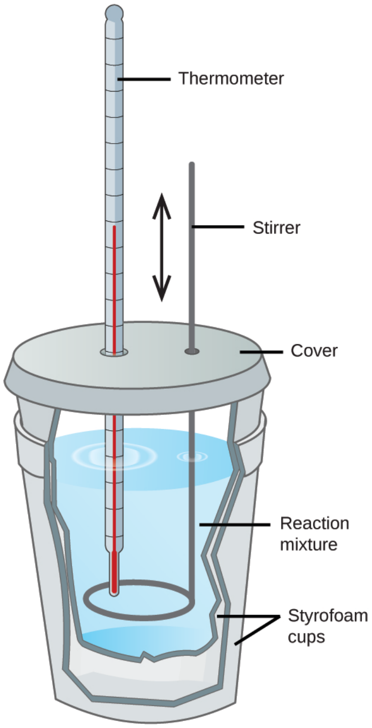


Figure 4.3b A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, a motorized stirring mechanism, and a more accurate temperature sensor (Figure 4.3c).

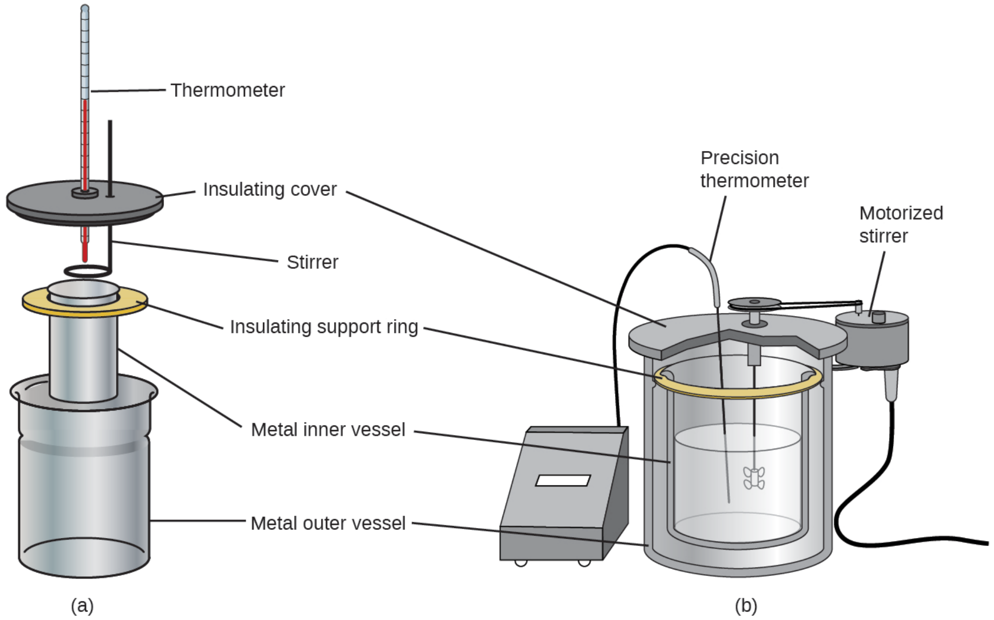


Figure 4.3c Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 4.3d). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{\text{substance M}}$ and $q_{\text{substance W}}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{\text{substance M}}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W (M is "losing" heat, while W "gains/aborbs" the heat).

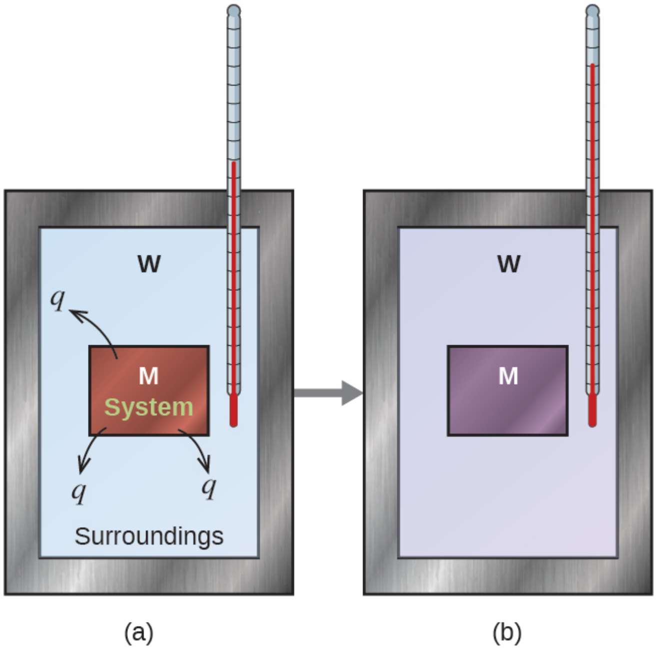


Figure 4.3d In a simple calorimetry process, (a) heat, *q*, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 4.3a

Heat Transfer between Substances at Different Temperatures

A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table 4.2a), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then *heat given off by rebar = −heat taken in by water*, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f, rebar}} - T_{\text{i, rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f, water}} - T_{\text{i, water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g}\ ^\circ\text{C})(360\ \text{g})(42.7\ ^\circ\text{C} - T_{\text{i, rebar}}) = (4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7\ ^\circ\text{C} - 24.0\ ^\circ\text{C})$$

$$T_{\text{i, rebar}} = \frac{(4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7\ ^\circ\text{C} - 24.0\ ^\circ\text{C})}{(0.449\ \text{J/g}\ ^\circ\text{C})(360\ \text{g})} + 42.7\ ^\circ\text{C}$$

Solving this gives $T_{\text{i,rebar}}$= 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 4.3a

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Check Your Answer[1]

Exercise 4.3b

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Check Your Answer[2]

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example 4.3b

Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, *heat given off by metal = -heat taken in by water*, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f, metal}} - T_{\text{i, metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f, water}} - T_{\text{i, water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\ \text{g})(28.5\ ^{\circ}\text{C} - 100.0\ ^{\circ}\text{C}) = -(4.184\ \text{J/g}\ ^{\circ}\text{C})(60.0\ \text{g})(28.5\ ^{\circ}\text{C} - 22.0\ ^{\circ}\text{C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\ \text{J/g}\ ^{\circ}\text{C})(60.0\ \text{g})(6.5\ ^{\circ}\text{C})}{(59.7\ \text{g})(-71.5\ ^{\circ}\text{C})} = 0.38\ \text{J/g}\ ^{\circ}\text{C}$$

Comparing this with values in Table 4.2a, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 4.3c

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Check Your Answer[3]

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

This concept lies at the heart of all calorimetry problems and calculations.

Example 4.3c

Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M HCl(*aq*) and 50.0 mL of 0.10 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and its surroundings.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.18 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184\ \text{J/g}\ {}^\circ\text{C})(1.0 \times 10^2\ \text{g})(28.9\ {}^\circ\text{C} - 22.0\ {}^\circ\text{C}) = 2.89 \times 10^3\ \text{J}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.89 \times 10^3\ \text{J}$$

The negative sign indicates that the reaction is exothermic. It produces 2.89 kJ of heat.

Exercise 4.3d

When 100 mL of 0.200 M $NaCl$(*aq*) and 100 mL of 0.200 M $AgNO_3$(*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Check Your Answer[4]

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 4.3e). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$

(sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\mathrm{NaC_2H_3O_2}(aq) \longrightarrow \mathrm{NaC_2H_3O_2}(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused. The video below provides a visual representation of this process (no audio).

Watch: Precipitation reaction that occurs when the disk in a chemical hand warmer is flexed (21 seconds – no audio)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is $2\mathrm{Fe}(s) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$. Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

Example 4.3d

Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack” (Figure 4.3e). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of *q* for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.

Figure 4.3e An instant cold pack consists of a bag containing solid ammonium nitrate and the second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{\text{rxn}} = -q_{\text{soln}}$$

with “rxn” and “soln” used as shorthand for “reaction” and “solution,” respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned} q_{\text{rxn}} &= -q_{\text{soln}} = -(c \times m \times \Delta T)_{\text{soln}} \\ & -[(4.184 \text{ J/g } ^\circ\text{C}) \times (53.2 \text{ g}) \times (20.3 \text{ }^\circ\text{C} - 24.9 \text{ }^\circ\text{C})] \\ & -[(4.184 \text{ J/g } ^\circ\text{C}) \times (53.2 \text{ g}) \times (-4.6 \text{ }^\circ\text{C})] \\ & +1.0 \times 10^3 \text{ J} = +1.0 \text{ kJ} \end{aligned}$$

The positive sign for *q* indicates that the dissolution is an endothermic process.

Exercise 4.3e

When a 3.00-g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Check Your Answer[5]

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a **bomb calorimeter**, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure 4.3f). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is trapped in the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known *q*, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.

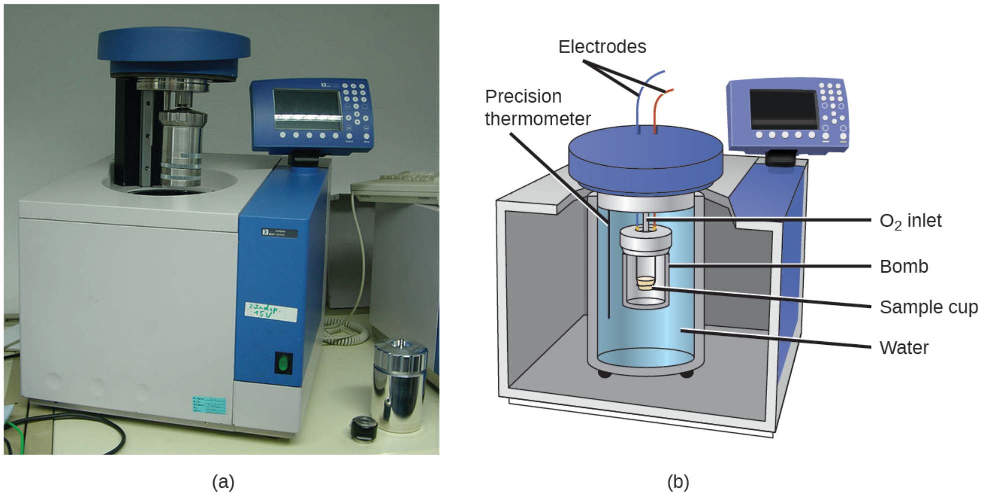


Figure 4.3f (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by Harbor1, CC BY 3.0)

Watch What is a calorie? Emma Bryce (5 mins)

Watch Physical Chemistry iBook – Bomb Calorimetry (3 min)

Example 4.3e

Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\ & -[(4.184\ \text{J/g}\ ^\circ\text{C}) \times (775\ \text{g}) \times (35.6\ ^\circ\text{C} - 23.8\ ^\circ\text{C}) + 893\ \text{J}/^\circ\text{C} \times (35.6\ ^\circ\text{C} - 23.8\ ^\circ\text{C})] \\ & -(38,300\ \text{J} + 10,500\ \text{J}) \\ & -48,800\ \text{J} = -48.8\ \text{kJ} \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

Exercise 4.3f

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Check Your Answer[6]

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[7] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, with different dietary regimes, and different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A **nutritional calorie (Calorie)** is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Exercise 4.3g

Check Your Learning Exercise (Text Version)
If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in the above figure 4.3b, what is the resulting temperature of the water?

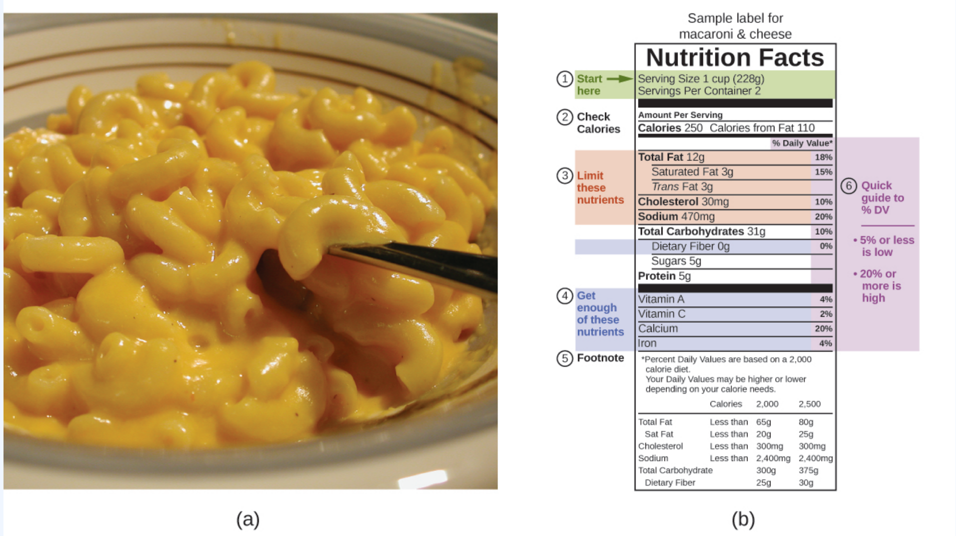
Check Your Answer[8]

Source: “Exercise 4.3g” is adapted from “Exercise 9.2-10” in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure 4.3g).



Nutrition Facts

Serving Size 1 cup (228g)
Servings Per Container 2

Amount Per Serving
Calories 250 Calories from Fat 110

	% Daily Value*
Total Fat 12g	18%
Saturated Fat 3g	15%
Trans Fat 3g	
Cholesterol 30mg	10%
Sodium 470mg	20%
Total Carbohydrates 31g	10%
Dietary Fiber 0g	0%
Sugars 5g	
Protein 5g	
Vitamin A	4%
Vitamin C	2%
Calcium	20%
Iron	4%

*Percent Daily Values are based on a 2,000 calorie diet.
Your Daily Values may be higher or lower depending on your calorie needs.

	Calories	2,000	2,500
Total Fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2,400mg	2,400mg
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

Figure 4.3g (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food’s nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by Rex Roof, CC BY 2.0; credit b: *Chemistry (OpenStax)*, CC BY 4.0).

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5\text{ g protein} \times 4\text{ Calories/g}) + (31\text{ g carb} \times 4\text{ Calories/g}) + (12\text{ g fat} \times 9\text{ Calories/g}) = 252\text{ Calories}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the **Atwater system** that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by the bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fibre content, which is an indigestible carbohydrate. To determine the energy content of food, the quantities of carbohydrates, protein, and fat are each multiplied by the average Calories per gram for each, and the products are summed to obtain the total energy.

Access The US Department of Agriculture (USDA) National Nutrient Database, containing nutritional information on over 8000 foods.

Exercise 4.3h

Check Your Learning Exercise (Text Version)
The amount of fat recommended for someone with a daily diet of 2000 Calories is 65g. What percentage of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g?

Check Your Answer[9]

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Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “9.2 Calorimetry” In *General*

Notes

1. The final temperature (reached by both copper and water) is 38.8 °C.
2. The final temperature (reached by both copper and water) is 38.8 °C.
3. c_{metal}= 0.13 J/g °C
   This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.
4. 1.34×10^3 J; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water
5. 1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water
6. 39.0 kJ
7. Francis D. Reardon et al. “The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics.” *Medical and Biological Engineering and Computing* 8 (2006)721–28, http://link.springer.com/article/10.1007/s11517-006-0086-5.
8. 38.5 °C
9. 30%

4.4 ENTHALPY

Learning Objectives

By the end of this section, you will be able to:

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of **chemical thermodynamics**, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the **internal energy (*U*)**, sometimes symbolized as *E*.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (q) from the surroundings or when the surroundings do work (w) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w$$

as shown in Figure 4.4a. This is one version of the **first law of thermodynamicsinternal energy (*U*)**, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

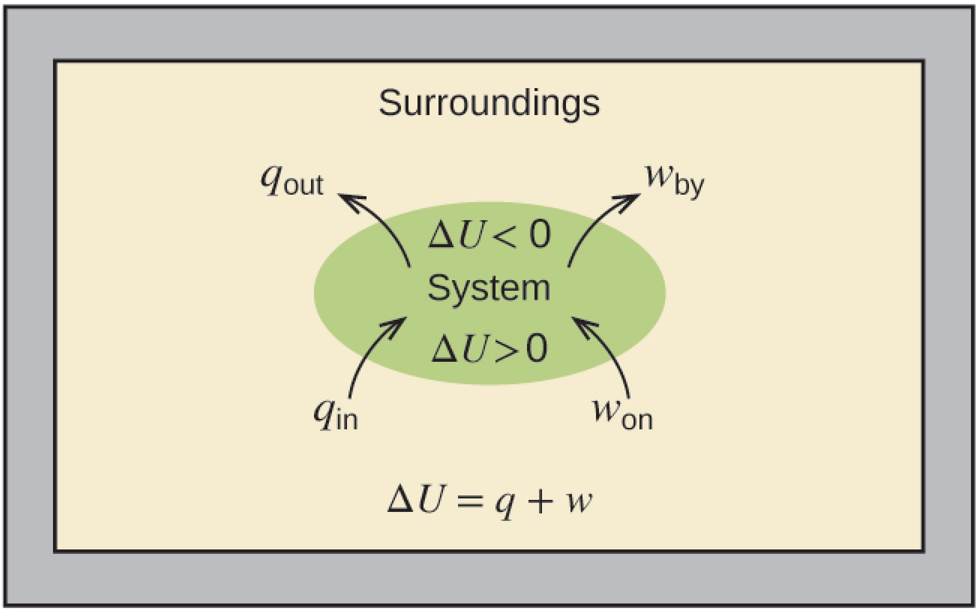

Figure 4.4a Relationship between Internal energy, U, Work, w and Heat Flow, q (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A type of work called **expansion work** (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work by pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics

Energy Conversion

This view of an internal combustion engine illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into the energy of motion.

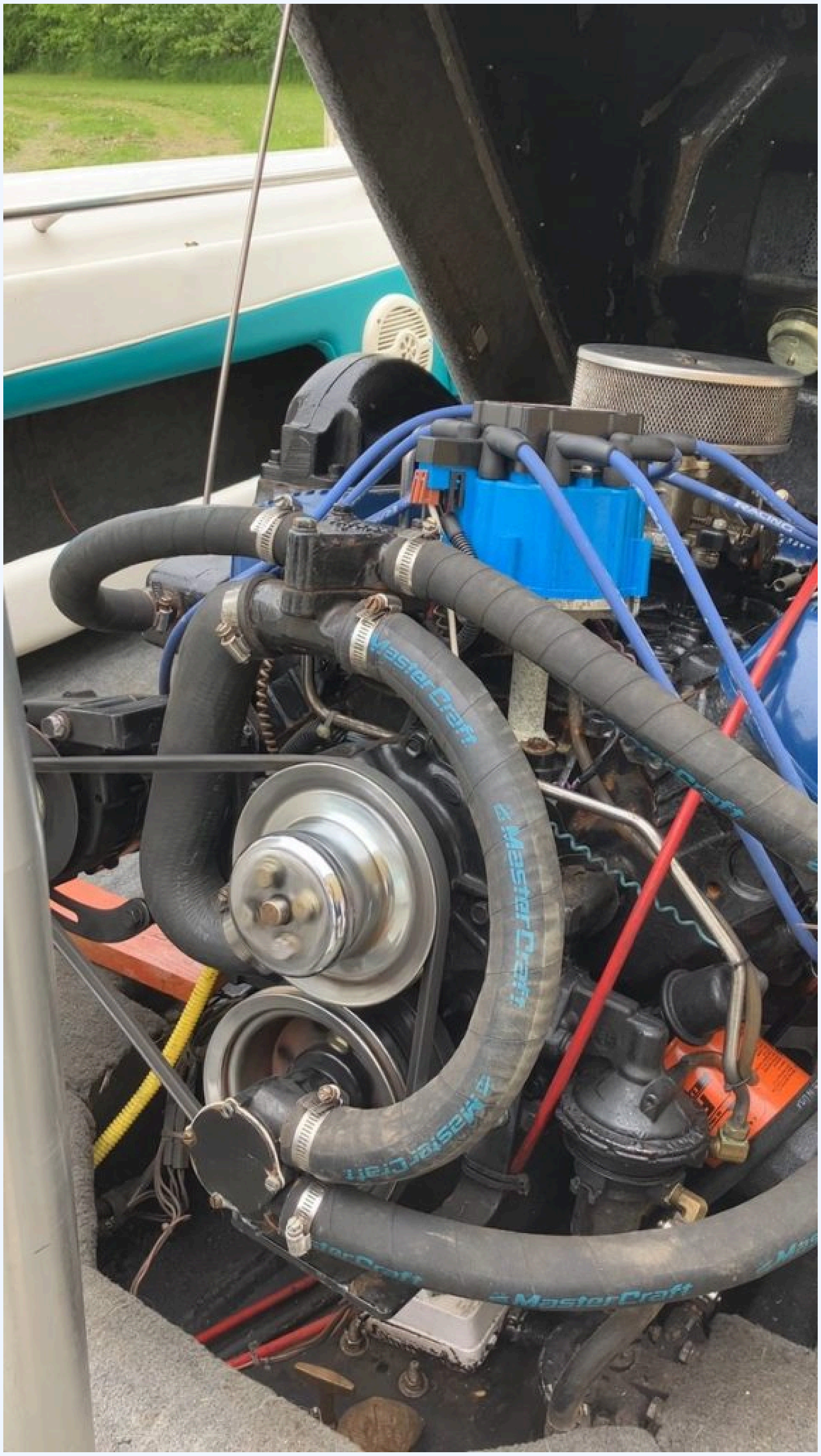

Figure 4.4b An internal combustion engine converts chemical energy into mechanical energy through the breaking of chemical bonds. (credit: photo by J.R. van Haarlem, CC-BY 4.0)

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a **state function** (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 4.4b). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

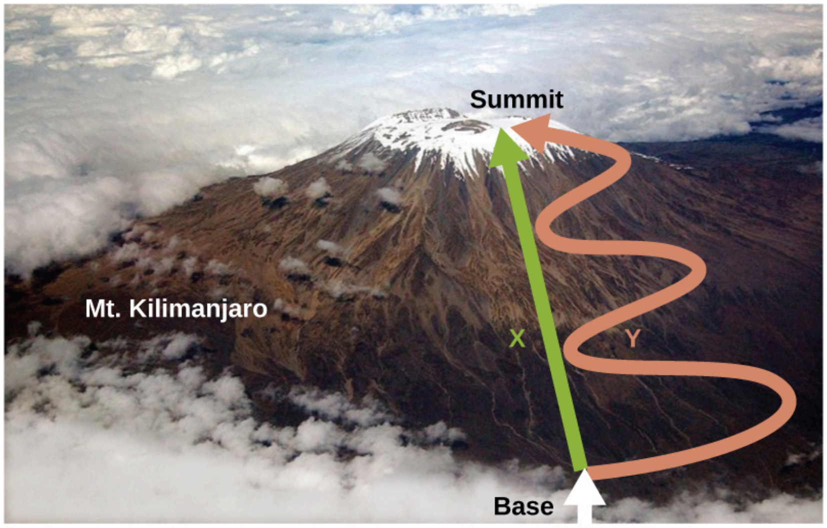

Figure 4.4c Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on the path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner, CC BY 2.0)

Chemists ordinarily use a property known as **enthalpy (*H*)** to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (U) and the mathematical product of its pressure (P) and volume (V):

$$H = U + PV$$

Since it is derived from three state functions (U, P, and V), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the **enthalpy change (Δ*H*)** is:

$$\Delta H = \Delta U + P\Delta V$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will always be opposite:

$$P\Delta V = -w$$

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

$$\begin{aligned} \Delta H &= \Delta U + P\Delta V \\ \\ & q_{\text{p}} + w - w \\ \\ & q_{\text{p}} \end{aligned}$$

where q_{p} is the heat of reaction under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_{p}) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

   $$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l) \quad \Delta H = -286 \text{ kJ}$$

   This equation indicates that when 1 mole of hydrogen gas and $\frac{1}{2}$ mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

$$\begin{array}{ll}\text{(two-fold increase in amounts)} & \\ 2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l) & \Delta H = 2 \times (-286 \text{ kJ}) = -572 \text{ kJ} \\ & \\ \text{(two-fold decrease in amounts)} & \\ \frac{1}{2}\text{H}_2(g) + \frac{1}{4}\text{O}_2(g) \longrightarrow \frac{1}{2}\text{H}_2\text{O}(l) & \Delta H = \frac{1}{2} \times (-286 \text{ kJ}) = -143 \text{ kJ}\end{array}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and $\frac{1}{2}$ mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(g) \qquad \Delta H = -242 \text{ kJ}$$

3. A negative value of an enthalpy change, ΔH, indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Example 4.4a

Measurement of an Enthalpy Change

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. What is Δ*H*, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described in Example 4.3c in Chapter 4.3 Calorimetry?

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. This ratio $\frac{-2.9 \text{ kJ}}{0.0500 \text{ mol HCl}}$ can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H = 1 \cancel{\text{mol HCl}} \times \frac{-2.9 \text{ kJ}}{0.0500 \cancel{\text{mol HCl}}} = -58 \text{ kJ}$$

The enthalpy change when 1 mole of HCl reacts is −58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \qquad \Delta H = -58\ \mathrm{kJ}$$

Exercise 4.4a

When 1.34 g Zn(*s*) reacts with 60.0 mL of 0.750 M HCl(*aq*), 3.14 kJ of heat is produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

$$\mathrm{Zn}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g)$$

Check Your Answer[1]

Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction. Refer to Chapter 9 for a more detailed explanation.

Example 4.4b

Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

$$\mathrm{C_{12}H_{22}O_{11}}(aq) + 8\mathrm{KClO_3}(aq) \longrightarrow 12\mathrm{CO_2}(g) + 11\mathrm{H_2O}(l) + 8\mathrm{KCl}(aq).$$

Solution

We have $2.67\ \cancel{\mathrm{g}} \times \dfrac{1\ \mathrm{mol}}{342.3\ \cancel{\mathrm{g}}} = 0.00780\ \mathrm{mol}\ \mathrm{C_{12}H_{22}O_{11}}$ available, and

$7.19\ \cancel{\mathrm{g}} \times \dfrac{1\ \mathrm{mol}}{122.5\ \cancel{\mathrm{g}}} = 0.0587\ \mathrm{mol}\ \mathrm{KClO_3}$ available. Since

$0.0587 \text{ mol KClO}_3 \times \dfrac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{8 \text{ mol KClO}_3} = 0.00734 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$ is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant.

The reaction uses 8 mol $KClO_3$, and the conversion factor is $\dfrac{-43.7 \text{ kJ}}{0.0587 \text{ mol KClO}_3}$, so we have $\Delta H = 8 \text{ mol} \times \dfrac{-43.7 \text{ kJ}}{0.0587 \text{ mol KClO}_3} = -5960 \text{ kJ}$. The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} + 8\text{KClO}_3 \longrightarrow 12\text{CO}_2 + 11\text{H}_2\text{O} + 8\text{KCl} \qquad \Delta H = -5960 \text{ kJ}$$

Exercise 4.4b

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_2(s)$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2(s)$ is produced?

Check Your Answer[2]

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A **standard state** is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate the standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol (ΔH°_{298}) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes.

Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property-specific heat from the extensive property heat capacity, as seen previously.)

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH_C°) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$\mathrm{C_2H_5OH}(l) + 3\mathrm{O_2}(g) \longrightarrow 2\mathrm{CO_2} + 3\mathrm{H_2O}(l) \qquad \Delta H^\circ_{298} = -1366.8 \text{ kJ}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 4.4a. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and **hydrocarbons** (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table 4.4a Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion, $\Delta H_c^\circ\,(\frac{\text{kJ}}{\text{mol}}\text{ at }25\,^\circ\text{C})$
carbon	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5
hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	−601.6
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	−296.8
carbon monoxide	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	−283.0
methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−890.8
acetylene	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	−1301.1
ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1366.8
methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$	−5461

Example 4.4c

Using Enthalpy of Combustion

As Figure 4.4d suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.

Figure 4.4d The combustion of gasoline is very exothermic. (credit: modification of work by AlexEagle, CC BY 2.0)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 4.4a gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \cancel{\text{L C}_8\text{H}_{18}} \times \frac{1000\ \cancel{\text{mL C}_8\text{H}_{18}}}{1\ \cancel{\text{L C}_8\text{H}_{18}}} \times \frac{0.692\ \cancel{\text{g C}_8\text{H}_{18}}}{1\ \cancel{\text{mL C}_8\text{H}_{18}}} \times \frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114\ \cancel{\text{g C}_8\text{H}_{18}}} \times \frac{-5460\ \text{kJ}}{1\ \cancel{\text{mol C}_8\text{H}_{18}}} = -3.31 \times 10^4\,\text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$1.00\ \text{L C}_8\text{H}_{18} \longrightarrow 1.00 \times 10^3\ \text{mL C}_8\text{H}_{18}$$

$$1.00 \times 10^3\ \text{mL C}_8\text{H}_{18} \longrightarrow 692\ \text{g C}_8\text{H}_{18}$$

$$692\ \text{g C}_8\text{H}_{18} \longrightarrow 6.07\ \text{mol C}_8\text{H}_{18}$$

$$692\ \text{g C}_8\text{H}_{18} \longrightarrow -3.31 \times 10^4\,\text{kJ}$$

Exercise 4.4c

How much heat is produced by the combustion of 125 g of acetylene?

Check Your Answer[3]

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 4.4d). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of **biofuel** per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.

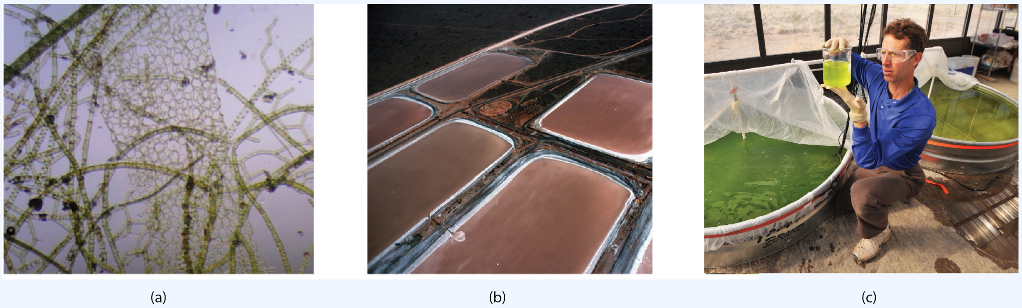

Figure 4.4e (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig, CC BY 2.0; credit b: modification of work by Robert Kerton/CSIRO, CC BY 3.0; credit c: work by Sandia Labs, CC BY-NC-ND 2.0)

According to the US Department of Energy, only 39,000 square kilometres (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under \$36.5 per gallon.[4] The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure 4.4e).

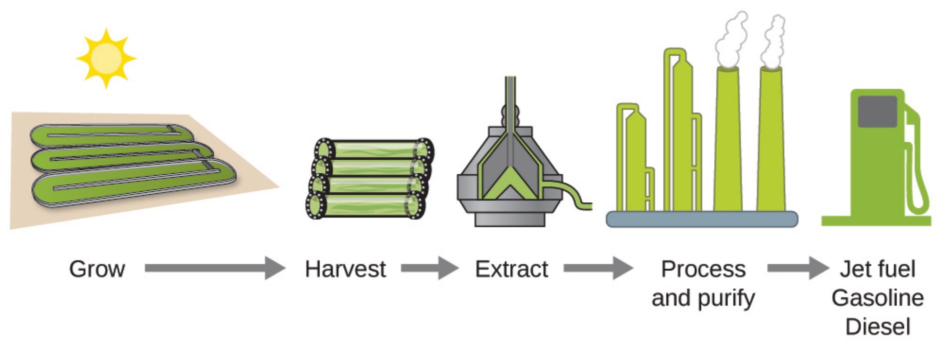

Figure 4.4f Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch Algae for Fuel – a QUEST Nebraska Feature (8 mins)

Standard Enthalpy of Formation

A **standard enthalpy of formation** ΔH_f° is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta H_\text{f}^\circ = \Delta H_{298}^\circ = -393.5\ \text{kJ}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $NO_2(g)$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^\circ = \Delta H_{298}^\circ = +33.2 \text{ kJ}$$

A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, NO_2(*g*).

You will find a table of standard enthalpies of the formation of many common substances in Appendix H. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example 4.4d

Evaluating an Enthalpy of Formation

Ozone, O_3(*g*), forms from oxygen, O_2(*g*), by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

$$3O_2(g) \longrightarrow 2O_3(g) \qquad \Delta H_{298}^\circ = +286 \text{ kJ}$$

Solution

ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for O_3(*g*) is the enthalpy change for the reaction:

$$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$$

For the formation of 2 mol of O_3(*g*), $\Delta H_{298}^\circ = +286 \text{ kJ}$. This ratio, $\left(\frac{286 \text{ kJ}}{2 \text{ mol } O_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of O_3(*g*) is formed, which is the enthalpy of formation for O_3(*g*):

$$\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1 \cancel{\text{mol } O_3} \times \frac{286 \text{ kJ}}{2 \cancel{\text{mol } O_3}} = 143 \text{ kJ}$$

Therefore, $\Delta H_f^\circ[O_3(g)] = +143 \text{ kJ/mol}$.

Exercise 4.4d

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, HCl(*g*). What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of the formation of HCl(*g*) is −92.3 kJ/mol.

Check Your Answer[5]

Example 4.4e

Writing Reaction Equations for $\Delta H_{\mathrm{f}}^{\circ}$

Write the heat of formation reaction equations for:

a. $C_2H_5OH(l)$
b. $Ca_3(PO_4)_2(s)$

Solution

Remembering that $\Delta H_{\mathrm{f}}^{\circ}$ reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $$2\mathrm{C}(s,\ \text{graphite}) + 3\mathrm{H}_2(g) + \frac{1}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{C}_2\mathrm{H}_5\mathrm{OH}(l)$$

b. $$3\mathrm{Ca}(s) + \frac{1}{2}\mathrm{P}_4(s) + 4\mathrm{O}_2(g) \longrightarrow \mathrm{Ca}_3(\mathrm{PO}_4)_2(s)$$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 4.4e

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_5(l)$
b. $Na_2CO_3(s)$

Check Your Answer[6]

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of **Hess's law**, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps*. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or through a two-step process. The direct process is written:

$$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H^\circ_{298} = -394\ \mathrm{kJ}$$

In the two-step process, first carbon monoxide is formed:

$$\mathrm{C}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g) \qquad \Delta H^\circ_{298} = -111\ \mathrm{kJ}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H^\circ_{298} = -283\ \mathrm{kJ}$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\text{Step 1: } C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

$$\text{Step 2: } CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

$$\text{Sum: } C(s) + \frac{1}{2}O_2(g) + CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + CO_2(g)$$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 4.4a to find the enthalpy change of the entire reaction from its two steps:

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H^\circ_{298} = -111 \text{ kJ}$$

$$\begin{array}{ll} CO(g)+\frac{1}{2}O_2(g)\longrightarrow CO_2(g) & \Delta H^\circ_{298}=-283 \text{ kJ} \\ \hline C(s)+O_2(g)\longrightarrow CO_2(g) & \Delta H^\circ_{298}=-394 \text{ kJ} \end{array}$$

The result is shown in Figure 4.4g. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

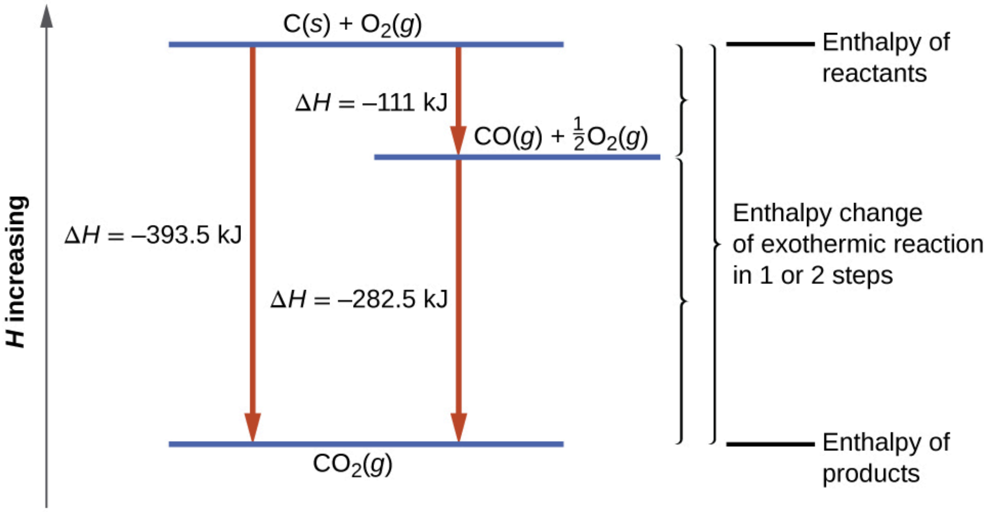

Figure 4.4g The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than the reactants (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

   $$\frac{1}{2}\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \qquad \Delta H = +33.2\ \mathrm{kJ}$$

   When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

   $$\mathrm{N_2}(g) + 2\mathrm{O_2}(g) \longrightarrow 2\mathrm{NO_2}(g) \qquad \Delta H = +66.4\ \mathrm{kJ}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

   $$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\mathrm{HCl}(g) \qquad \Delta H = -184.6\ \mathrm{kJ}$$

   Then, for the "reverse" reaction, the enthalpy change is also "reversed":

   $$2\mathrm{HCl}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) \qquad \Delta H = +184.6\ \mathrm{kJ}$$

Example 4.4f

Stepwise Calculation of $\Delta H_\mathrm{f}^\circ$ Using Hess's Law

Determine the enthalpy of formation, $\Delta H_\mathrm{f}^\circ$, of $FeCl_3(s)$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) \qquad \Delta H^\circ = -341.8\ \mathrm{kJ}$$

$$\mathrm{FeCl_2}(s) + \tfrac{1}{2}\mathrm{Cl}(g) \longrightarrow \mathrm{FeCl_3}(s) \qquad \Delta H^\circ = -57.7\ \mathrm{kJ}$$

Solution

We are trying to find the standard enthalpy of formation of $FeCl_3(s)$, which is equal to ΔH° for the reaction:

$$\mathrm{Fe}(s) + \frac{3}{2}\mathrm{Cl}(g) \longrightarrow \mathrm{FeCl_3}(s) \qquad \Delta H_\mathrm{f}^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find Δ*H*° is the sum of the two reactions with known Δ*H* values, so we must sum their Δ*H*s:

$$\mathrm{Fe}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) \quad \Delta H^\circ = -341.8\ \mathrm{kJ}$$

$$\frac{\mathrm{FeCl_2}(s)+\frac{1}{2}\mathrm{Cl_2}(g)\longrightarrow\mathrm{FeCl_3}(s)}{\mathrm{Fe}(s)+\frac{1}{2}\mathrm{Cl_2}(g)\longrightarrow\mathrm{FeCl_3}(s)} \qquad \frac{\Delta H^\circ=-57.7\ \mathrm{kJ}}{\Delta H^\circ=-399.5\ \mathrm{kJ}}$$

The enthalpy of formation, $\Delta H^\circ_\mathrm{f}$, of $FeCl_3$(*s*) is −399.5 kJ/mol.

Exercise 4.4f

Calculate Δ*H* for the process:

$$\mathrm{N_2}(g) + 2\mathrm{O_2}(g) \longrightarrow 2\mathrm{NO_2}(g)$$

from the following information:

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{NO}(g) \quad \Delta H = 180.5\ \mathrm{kJ}$$

$$\mathrm{NO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H = -57.06\ \mathrm{kJ}$$

Check Your Answer[7]

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of Δ*H*) if they are difficult to determine experimentally.

Example 4.4g

A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

i. $\mathrm{ClF_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{ClF_3}(g) \quad \Delta H^\circ = ?$

Use the reactions here to determine the Δ*H*° for reaction *(i)*:

ii. $2\text{OF}_2(g) \longrightarrow \text{O}_2(g) + 2\text{F}_2(g) \qquad \Delta H^\circ_{(ii)} = -49.4\ \text{kJ}$

iii. $2\text{ClF}(g) + \text{O}_2(g) \longrightarrow \text{Cl}_2\text{O}(g) + \text{OF}_2(g) \qquad \Delta H^\circ_{(iii)} = +205.6\ \text{kJ}$

iv. $\text{ClF}_3(g) + \text{O}_2(g) \longrightarrow \frac{1}{2}\text{Cl}_2\text{O}(g) + \frac{3}{2}\text{OF}_2(g) \qquad \Delta H^\circ_{(iv)} = +266.7\ \text{kJ}$

Solution

Our goal is to manipulate and combine reactions *(ii)*, *(iii)*, and *(iv)* such that they add up to reaction *(i)*. Going from left to right in *(i)*, we first see that ClF(*g*) is needed as a reactant. This can be obtained by multiplying reaction *(iii)* by $\frac{1}{2}$, which means that the Δ*H*° change is also multiplied by $\frac{1}{2}$:

$$\text{ClF}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \frac{1}{2}\text{Cl}_2\text{O}(g) + \frac{1}{2}\text{OF}_2(g) \qquad \Delta H^\circ = \frac{1}{2}(205.6) = +102.8\ \text{kJ}$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction *(ii)*, which means that the Δ*H*° changes sign and is halved:

$$\frac{1}{2}\text{O}_2(g) + \text{F}_2(g) \longrightarrow \text{OF}_2(g) \qquad \Delta H^\circ = +24.7\ \text{kJ}$$

To get ClF_3 as a product, reverse *(iv)*, changing the sign of Δ*H*°:

$$\frac{1}{2}\text{Cl}_2\text{O}(g) + \frac{3}{2}\text{OF}_2(g) \longrightarrow \text{ClF}_3(g) + \text{O}_2(g) \qquad \Delta H^\circ = -266.7\ \text{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{array}{ll}
\text{ClF}(g) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \tfrac{1}{2}\text{Cl}_2\text{O}(g) + \tfrac{1}{2}\text{OF}_2(g) & \Delta H^\circ = +102.8\ \text{kJ} \\
\tfrac{1}{2}\text{O}(g) + \text{F}_2(g) \longrightarrow \text{OF}_2(g) & \Delta H^\circ = +24.7\ \text{kJ} \\
\tfrac{1}{2}\text{Cl}_2\text{O}(g) + \tfrac{3}{2}\text{OF}_2(g) \longrightarrow \text{ClF}_3(g) + \text{O}_2(g) & \Delta H^\circ = -266.7\ \text{kJ} \\
\hline
\text{ClF}(g) + \text{F}_2 \longrightarrow \text{ClF}_3(g) & \Delta H^\circ = -139.2\ \text{kJ}
\end{array}$$

Reactants $\frac{1}{2}\text{O}_2$ and $\frac{1}{2}\text{O}_2$ cancel out product O_2; product $\frac{1}{2}\text{Cl}_2\text{O}$ cancels reactant $\frac{1}{2}\text{Cl}_2\text{O}$; and reactant $\frac{3}{2}\text{OF}_2$ is cancelled by products $\frac{1}{2}\text{OF}_2$ and OF_2. This leaves only reactants ClF(*g*) and F_2(*g*) and product ClF_3(*g*), which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified Δ*H*° values will give the desired Δ*H*°:

$$\Delta H^\circ = (+102.8\ \text{kJ}) + (24.7\ \text{kJ}) + (-266.7\ \text{kJ}) = -139.2\ \text{kJ}$$

Exercise 4.4g

Aluminum chloride can be formed from its elements:

i. $2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s) \quad \Delta H^\circ = ?$

Use the reactions here to determine the Δ*H*° for reaction *(i)*:

ii. $HCl(g) \longrightarrow HCl(aq) \quad \Delta H^\circ_{(ii)} = -74.8 \text{ kJ}$

iii. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \quad \Delta H^\circ_{(iii)} = -185 \text{ kJ}$

iv. $AlCl_3(aq) \longrightarrow AlCl_3(s) \quad \Delta H^\circ_{(iv)} = +323 \text{ kJ/mol}$

v. $2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g) \quad \Delta H^\circ_{(v)} = -1049 \text{ kJ}$

Check Your Answer[8]

We also can use **Hess's law** to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with Σ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_{\text{f}}(\text{products}) - \sum n \times \Delta H^\circ_{\text{f}}(\text{reactants})$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 4.4h

Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g) \qquad \Delta H^\circ = ?$$

Solution: Using the Equation

Use the special form of Hess's law given previously:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_{\text{f}}(\text{products}) - \sum n \times \Delta H^\circ_{\text{f}}(\text{reactants})$$

$$= [2\ \cancel{\text{mol HNO}_3} \times \frac{-207.4\ \text{kJ}}{\cancel{\text{mol HNO}_3(aq)}} + 1\ \cancel{\text{mol NO}(g)} \times \frac{+90.2\ \text{kJ}}{\cancel{\text{mol NO}(g)}}]$$

$$-[3\ \cancel{\text{mol NO}_2(g)} \times \frac{+33.2\ \text{kJ}}{\cancel{\text{mol NO}_2(g)}} + 1\ \cancel{\text{mol H}_2\text{O}(l)} \times \frac{+285.8\ \text{kJ}}{\cancel{\text{mol H}_2\text{O}(l)}}]$$

$$= 2(-207.4\ \text{kJ}) + 1(+90.2\ \text{kJ}) - 3(+33.2\ \text{kJ}) - 1(-285.8\ \text{kJ})$$

$$= -138.4\ \text{kJ}$$

Solution: Supporting Why the General Equation Is Valid

Alternatively, we can write this reaction as the sum of the decompositions of 3NO2(*g*) and 1H2O(*l*) into their constituent elements, and the formation of 2HNO3(*aq*) and 1NO(*g*) from their constituent elements. Writing out these reactions, and noting their relationships to the $\Delta H^\circ_{\text{f}}$ values for these compounds (from Appendix H), we have:

$$3NO_2(g) \longrightarrow 3/2N_2(g) + 3O_2(g) \qquad \Delta H^\circ_1 = -99.6\ \text{kJ}$$

$$H_2O \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\circ_2 = +285.8\ \text{kJ}\ [-1 \times \Delta H^\circ_{\text{f}}(H_2O)]$$

$$H_2(g) + N_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow 2HNO_3(aq) \qquad \Delta H^\circ_3 = -414.8\ \text{kJ}\ [2 \times \Delta H^\circ_{\text{f}}(HNO_3)]$$

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO(g) \qquad \Delta H^\circ_4 = +90.2\ \text{kJ}\ [1 \times (NO)]$$

Summing these reaction equations gives the reaction we are interested in:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\Delta H^\circ_{\text{rxn}} \quad \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 = (-99.6\ \text{kJ}) + (+285.8\ \text{kJ}) + (-414.8\ \text{kJ}) + (+90.2\ \text{kJ})$$

$$-138.4\ \text{kJ}$$

So the standard enthalpy change for this reaction is Δ*H*° = −138.4 kJ.

Note that this result was obtained by (1) multiplying the $\Delta H_{\mathrm{f}}^{\circ}$ of each product by its stoichiometric coefficient and summing those values, (2) multiplying the $\Delta H_{\mathrm{f}}^{\circ}$ of each reactant by its stoichiometric coefficient and summing those values, and then (3) subtracting the result found in (2) from the result found in (1). This is also the procedure in using the general equation, as shown.

Exercise 4.4h

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(\mathit{l})$, when $H_2O(\mathit{l})$ and $CO_2(\mathit{g})$ are formed. Use the following enthalpies of formation: $C_2H_5OH(\mathit{l})$, −278 kJ/mol; $H_2O(\mathit{l})$, −286 kJ/mol; and $CO_2(\mathit{g})$, −394 kJ/mol.

Check Your Answer[9]

Exercise 4.4i

Check Your Learning Exercise (Text Version)
When 2.50 g of methane burns in oxygen, 125kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

Check Your Answer[10]

Source: "Exercise 4.4i" is adapted from "Exercise 8.3-11" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Key Equations

- $\Delta U = q + w$
- $\Delta H_{\text{reaction}}^{\circ} = \sum n \times \Delta H_{\mathrm{f}}^{\circ}(\text{products}) - \sum n \times \Delta H_{\mathrm{f}}^{\circ}(\text{reactants})$

Attribution & References

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Notes

1. $\Delta H = -153$ kJ
2. $\Delta H = -338$ kJ
3. 6.25×10^3 kJ
4. For more on algal fuel, see Algae to solve the Pentagon's jet fuel problem [New tab] in *The Guardian*.
5. For the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H^\circ_{298} = -184.6\ \text{kJ}$
6. (a) $4C(s,\ \text{graphite}) + 5H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OC_2H_5(l)$; (b) $2Na(s) + C(s,\ \text{graphite}) + \frac{3}{2}O_2(s) \longrightarrow Na_2CO_3(s)$
7. 66.4 kJ
8. −1407 kJ
9. −1368 kJ/mol
10. -802 kJ / mol

CHAPTER 4 - SUMMARY

4.1 Physical and Chemical Properties

All substances have distinct physical and chemical properties, and may undergo physical or chemical changes. Physical properties, such as hardness and boiling point, and physical changes, such as melting or freezing, do not involve a change in the composition of matter. Chemical properties, such flammability and acidity, and chemical changes, such as rusting, involve production of matter that differs from that present beforehand.

Measurable properties fall into one of two categories. Extensive properties depend on the amount of matter present, for example, the mass of gold. Intensive properties do not depend on the amount of matter present, for example, the density of gold. Heat is an example of an extensive property, and temperature is an example of an intensive property.

4.2 Energy Basics

Energy is the capacity to supply heat or do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics).

The thermal energy of matter is due to the kinetic energies of its constituent atoms or molecules. Temperature is an intensive property of matter reflecting hotness or coldness that increases as the average kinetic energy increases. Heat is the transfer of thermal energy between objects at different temperatures. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J).

Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

4.3 Calorimetry

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations.

Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

ΔHf°

4.4 Enthalpy

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or ΔH° for reactions occurring under standard state conditions at 298 K. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. The standard enthalpy of formation, ΔHf°, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar and 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

Attribution & References

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CHAPTER 4 - REVIEW

4.1 Physical and Chemical Properties

1. Classify the six bolded properties (also marked before/after by *) in the following paragraph as chemical or physical:Fluorine is a pale yellow ***gas*** that ***reacts with most substances***. The free element ***melts at −220 °C*** and ***boils at −188 °C***. Finely divided ***metals burn in fluorine*** with a bright flame. ***Nineteen grams of fluorine will react with 1.0 gram of hydrogen.***
2. Classify each of the following changes as physical or chemical:
   1. condensation of steam
   2. burning of gasoline
   3. souring of milk
   4. dissolving of sugar in water
   5. melting of gold

   Check answers: [1]
3. Classify each of the following changes as physical or chemical:
   1. coal burning
   2. ice melting
   3. mixing chocolate syrup with milk
   4. explosion of a firecracker
   5. magnetizing of a screwdriver
4. The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?
   Check answers: [2]
5. A 2.0-litre volume of hydrogen gas combined with 1.0 litre of oxygen gas to produce 2.0 litres of water vapour. Does oxygen undergo a chemical or physical change?
6. Explain the difference between extensive properties and intensive properties. **Check answers:** [3]
7. Identify the following properties as either extensive or intensive.
   1. volume
   2. temperature
   3. humidity
   4. heat
   5. boiling point
8. The density (d) of a substance is an intensive property that is defined as the ratio of its mass (m) to its

volume (V).

$$\text{density} = \frac{\text{mass}}{\text{volume}}\ \text{d} = \frac{\text{m}}{\text{V}}$$

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive. **Check answers:** [4]

4.2 Energy Basics

1. A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?
   Check answers: [5]
2. Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.
3. Explain the difference between heat capacity and specific heat of a substance.
   Check answers: [6]
4. Calculate the heat capacity, in joules and in calories per degree, of the following:
   a. 28.4 g of water
   b. 1.00 oz of lead
5. Calculate the heat capacity, in joules and in calories per degree, of the following:
   a. 45.8 g of nitrogen gas
   b. 1.00 pound of aluminum metal
   c. **Check answers:** [7]
6. How much heat, in joules and in calories, must be added to a 75.0–g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?
7. How much heat, in joules and in calories, is required to heat a 28.4-g (1 oz) ice cube from −23.0 °C to −1.0 °C? **Check answers:** [8]
8. How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?
9. If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?
   Check answers: [9]
10. A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.
    a. What is the specific heat of the substance?
    b. If it is one of the substances found in Table 4.2a, what is its likely identity?
11. A piece of an unknown solid substance weighs 437.2 g and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.
    a. What is the specific heat of the substance?
    b. If it is one of the substances found in Table 4.2a, what is its likely identity?

    Check answers: [10]

12. An aluminum kettle weighs 1.05 kg.
    a. What is the heat capacity of the kettle?
    b. How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?
    c. How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and specific heat of 4.184 J/g °C)?
13. Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?
    Check answers: [11]

4.3 Calorimetry

1. A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.
2. Would the amount of heat measured for the reaction in Example 3 be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.
    Check answers: [12]
3. Would the amount of heat absorbed by the dissolution in Example 4 appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.
4. Would the amount of heat absorbed by the dissolution in Example 4 appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.
    Check answers: [13]
5. How many millilitres of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that

coffee and water have the same density and the same specific heat.
Check answers: [14]

6. How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.
7. A 45-g aluminum spoon (specific heat 0.88 J/g °C) at 24 °C is placed in 180 mL (180 g) of coffee at 85 °C and the temperature of the two becomes equal.(a) What is the final temperature when the two become equal? Assume that coffee has the same specific heat as water.(b) The first time a student solved this problem she got an answer of 88 °C. Explain why this is clearly an incorrect answer.
8. The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.
   Check answers: [15]
9. A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in Figure 2. The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?
10. If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure 2, what is the resulting temperature of the water?
    Check answers: [16]
11. A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter (Figure 2). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?
12. Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter (Figure 2) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?\
    Check answers: [17]
13. When 50.0 g of 0.200 M $NaCl(aq)$ at 24.1 °C is added to 100.0 g of 0.100 M $AgNO_3(aq)$ at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as $AgCl(s)$ forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.
14. The addition of 3.15 g of $Ba(OH)_2{\cdot}8H_2O$ to a solution of 1.52 g of NH_4SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:
    $Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(aq) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$
    Check answers: [18]

15. The reaction of 50 mL of acid and 50 mL of base described in Example 3 increased the temperature of the solution by 6.9 degrees. How much would the temperature have increased if 100 mL of acid and 100 mL of base had been used in the same calorimeter starting at the same temperature of 22.0 °C? Explain your answer.
16. If the 3.21 g of NH_4NO_3 in Example 4 were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.
    Check answers: [19]
17. When 1.0 g of fructose, $C_6H_{12}O_6(s)$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is q for this combustion?
18. When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?
    Check answers: [20]
19. One method of generating electricity is by burning coal to heat water, which produces steam that drives an electric generator. To determine the rate at which coal is to be fed into the burner in this type of plant, the heat of combustion per ton of coal must be determined using a bomb calorimeter. When 1.00 g of coal is burned in a bomb calorimeter (Figure 7), the temperature increases by 1.48 °C. If the heat capacity of the calorimeter is 21.6 kJ/°C, determine the heat produced by combustion of a ton of coal (2.000×10^3 pounds).
20. The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g?
    Check answers: [21]
21. A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?
22. What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g?
23. A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1×10^3 Calories if the average number of Calories for fat is 9.1 Calories/g?
    Check answers: [22]
24. A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?
25. Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs $4.23, or a liter of isooctane (density, 0.6919 g/mL) that costs $0.45? Compare the

nutritional value of the cereal with the heat produced by the combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

4.4 Enthalpy

1. Explain how the heat measured in Example 4.3c in Chapter 4.3 Calorimetry differs from the enthalpy change for the exothermic reaction described by the following equation:
$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$
2. Using the data in the check your learning section of Example 4.3c in Chapter 4.3 Calorimetry, calculate ΔH in kJ/mol of $\mathrm{AgNO_3}(aq)$ for the reaction:
$$\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq)$$
3. Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $\mathrm{NH_4NO_3}$ under the conditions described in Example 4.3d in Chapter 4.3 Calorimetry.
4. Calculate ΔH for the reaction described by the equation. (*Hint*: use the value for the approximate amount of heat absorbed by the reaction that you calculated in a previous exercise.)
$$\mathrm{Ba(OH)_2 \cdot 8H_2O}(s) + \mathrm{2NH_4SCN}(aq) \longrightarrow \mathrm{Ba(SCN)_2}(aq) + \mathrm{2NH_3}(aq) + \mathrm{10H_2O}(l)$$
5. Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $\mathrm{CaCl_2}$.
6. Although the gas used in an oxyacetylene torch (Figure 4.2f in Chapter 4.2 Energy Basics) is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in Table 4.4a. Considering the conditions for which the tabulated data are reported, suggest an explanation.
7. How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?
8. How much heat is produced by combustion of 125 g of methanol under standard state conditions?
9. How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?
10. What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?
11. When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?
12. How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?
$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \quad \Delta H^\circ_{298} = -58\ \mathrm{kJ}$ If both solutions are at the same temperature and the heat capacity of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?
13. A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter

increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

14. Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl_2F_2 (enthalpy of vaporization is 17.4 kJ/mol)?The vaporization reactions for SO_2 and CCl_2F_2 are $\mathrm{SO_2}(l) \longrightarrow \mathrm{SO_2}(g)$ and $\mathrm{CCl_2F}(l) \longrightarrow \mathrm{CCl_2F_2}(g)$, respectively.
15. Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.
16. Which of the enthalpies of combustion in Table 4.4a the table are also standard enthalpies of formation?
17. Does the standard enthalpy of formation of $H_2O(g)$ differ from $\Delta H°$ for the reaction $\mathrm{2H_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2H_2O}(g)$?
18. Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red $HgO(s)$ to $Hg(l)$ and $O_2(g)$ under standard conditions?
19. How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $Mn_3O_4(s)$ at standard state conditions?
20. How many kilojoules of heat will be released when exactly 1 mole of iron, Fe, is burned to form $Fe_2O_3(s)$ at standard state conditions?
21. The following sequence of reactions occurs in the commercial production of aqueous nitric acid: $\mathrm{4NH_3}(g) + \mathrm{5O_2}(g) \longrightarrow \mathrm{4NO}(g) + \mathrm{6H_2O}(l) \quad \Delta H = -907\ \mathrm{kJ}$ $\mathrm{2NO}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2NO_2}(g) \quad \Delta H = -113\ \mathrm{kJ}$ Determine the total $\mathrm{3NO_2} + \mathrm{H_2O} \longrightarrow \mathrm{2HNO_3}(aq) + \mathrm{NO}(g) \quad \Delta H = -139\ \mathrm{kJ}$ energy change for the production of one mole of aqueous nitric acid by this process.
22. Both graphite and diamond burn.$\mathrm{C}(s,\ \mathrm{diamond}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$For the conversion of graphite to diamond: $\mathrm{C}(s,\ \mathrm{graphite}) \longrightarrow \mathrm{C}(s,\ \mathrm{diamond}) \quad \Delta H^\circ_{298} = 1.90\ \mathrm{kJ}$ Which produces more heat, the combustion of graphite or the combustion of diamond?
23. From the molar heats of formation in Appendix H, determine how much heat is required to evaporate one mole of water: $\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$
24. Which produces more heat? $\mathrm{Os}(s) \longrightarrow \mathrm{2O_2}(g) \longrightarrow \mathrm{OsO_4}(s)or\mathrm{Os}(s) \longrightarrow \mathrm{2O_2}(g) \longrightarrow \mathrm{OsO_4}(g)$for the phase change $\mathrm{OsO_4}(s) \longrightarrow \mathrm{OsO_4}(g) \quad \Delta H = 56.4\ \mathrm{kJ}$
25. Calculate ΔH°_{298} for the process $\mathrm{Sb}(s) + \frac{5}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_5}(g)$from the following

$$\text{Sb}(s) + \tfrac{3}{2}\text{Cl}_2(g) \longrightarrow \text{SbCl}_3(g) \qquad \Delta H^\circ_{298} = -314 \text{ kJ}$$

information:

$$\text{SbCl}_3(s) + \text{Cl}_2(g) \longrightarrow \text{SbCl}_5(g) \quad \Delta H^\circ_{298} = -80 \text{ kJ}$$

26. Calculate ΔH°_{298} for the process $\text{Zn}(s) + \text{S}(s) + 2\text{O}_2(g) \longrightarrow \text{ZnSO}_4(s)$from the following

$$\text{Zn}(s) + \text{S}(s) \longrightarrow \text{ZnS}(s) \qquad \Delta H^\circ_{298} = -206.0 \text{ kJ}$$

information:

$$\text{ZnS}(s) + 2\text{O}_2(g) \longrightarrow \text{ZnSO}_4(s) \quad \Delta H^\circ_{298} = -776.8 \text{ kJ}$$

27. Calculate ΔH for the process $\text{Hg}_2\text{Cl}_2(s) \longrightarrow 2\text{Hg}(l) + \text{Cl}_2(g)$from the following information:

$$\text{Hg}(l) + \text{Cl}_2(g) \longrightarrow \text{HgCl}(s) \qquad \Delta H = -224 \text{ kJ}$$

$$\text{Hg}(l) + \text{HgCl}_2(s) \longrightarrow \text{Hg}_2\text{Cl}_2(s) \quad \Delta H = -41.2 \text{ kJ}$$

28. Calculate ΔH°_{298} for the process

$\text{Co}_3\text{O}_4(s) \longrightarrow 3\text{Co}(s) + 2\text{O}_2(g)$from the following information:

$$\text{Co}(s) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{CoO}(s) \qquad \Delta H^\circ_{298} = -237.9 \text{ kJ}$$

$$3\text{Co}(s) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{Co}_3\text{O}_4(s) \quad \Delta H^\circ_{298} = -177.5 \text{ kJ}$$

29. Calculate the standard molar enthalpy of formation of NO(*g*) from the following data:

$$\text{N}_2(g) + 2\text{O}_2 \longrightarrow 2\text{NO}_2(g) \qquad \Delta H^\circ_{298} = 66.4 \text{ kJ}$$

$$2\text{NO}(g) + \text{O}_2 \longrightarrow 2\text{NO}_2(g) \quad \Delta H^\circ_{298} = -114.1 \text{ kJ}$$

30. Using the data in Appendix H, calculate the standard enthalpy change for each of the following reactions:(a) $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$(b) $\text{Si}(s) + 2\text{Cl}_2(g) \longrightarrow \text{SiCl}_4(g)$(c) $\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \longrightarrow 2\text{Fe}(s) + 3\text{H}_2\text{O}(l)$(d) $2\text{LiOH}(s) + \text{CO}_2(g) \longrightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(g)$

31. Using the data in Appendix H, calculate the standard enthalpy change for each of the following reactions:(a) $\text{Si}(s) + 2\text{F}_2(g) \longrightarrow \text{SiF}_4(g)$(b) $2\text{C}(s) + 2\text{H}_2(g) \longrightarrow \text{CH}_3\text{CO}_2\text{H}(l)$(c) $\text{CH}_4(g) + \text{N}_2(g) \longrightarrow \text{HCN}(g) + \text{NH}_3(g)$(d) $\text{CS}_2(g) + 3\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(g)$

32. The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.(a) $2\text{Ag}_2\text{O}(s) \longrightarrow 4\text{Ag}(s) + \text{O}_2(g)$(b) $\text{SnO}(s) + \text{CO}(g) \longrightarrow \text{Sn}(s) + \text{CO}_2(g)$(c) $\text{Cr}_2\text{O}_3(s) + 3\text{H}_2(g) \longrightarrow 2\text{Cr}(s) + 3\text{H}_2\text{O}(l)$(d) $2\text{Al}(s) + \text{Fe}_2\text{O}_3(s) \longrightarrow \text{Al}_2\text{O}_3(s) + 2\text{Fe}(s)$

33. The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix H, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

$2H_2O_2(l) \longrightarrow 2H_2O(g) + O_2(g)$

Check answers: [23]

34. Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is −104 kJ/mol.
35. Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is −126 kJ/mol.

    Check answers: [24]
36. Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?
37. The white pigment TiO_2 is prepared by the reaction of titanium tetrachloride, $TiCl_4$, with water vapour in the gas phase: $TiCl_4(g) + 2H_2O(g) \longrightarrow TiO_2(s) + 4HCl(g)$.

    How much heat is evolved in the production of exactly 1 mole of $TiO_2(s)$ under standard state conditions?

    Check answers: [25]
38. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon: $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$.(a) Assuming that coke has the same enthalpy of formation as graphite, calculate ΔH°_{298} for this reaction.(b) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst: $2H_2 + CO(g) \longrightarrow CH_3OH(g)$.Under the conditions of the reaction, methanol forms as a gas. Calculate ΔH°_{298} for this reaction and for the condensation of gaseous methanol to liquid methanol.(c) Calculate the heat of combustion of 1 mole of liquid methanol to $H_2O(g)$ and $CO_2(g)$.
39. In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2. Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2:$CaC_2(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$ .Calculate the standard enthalpy of the reaction. The ΔH°_f of CaC_2 is −15.14 kcal/mol.

    Check answers: [26]
40. From the data in Table 2, determine which of the following fuels produces the greatest amount of heat per gram when burned under standard conditions: $CO(g)$, $CH_4(g)$, or $C_2H_2(g)$.
41. The enthalpy of combustion of hard coal averages −35 kJ/g, that of gasoline, 1.28×10^5 kJ/gal. How many kilograms of hard coal provide the same amount of heat as is available from 1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

    Check answers: [27]
42. Ethanol, C_2H_5OH, is used as a fuel for motor vehicles, particularly in Brazil.(a) Write the balanced equation for the combustion of ethanol to $CO_2(g)$ and $H_2O(g)$, and, using the data in Appendix H, calculate the enthalpy of combustion of 1 mole of ethanol.(b) The density of ethanol is 0.7893 g/mL.

Calculate the enthalpy of combustion of exactly 1 L of ethanol.(c) Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n–octane, C_8H_{18}(ΔH°_f = -208.4 kJ/mol; density = 0.7025 g/mL).

43. Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B_2H_6, produces $B_2O_3(s)$ and $H_2O(g)$], methane [CH_4, produces $CO_2(g)$ and $H_2O(g)$], and hydrazine [N_2H_4, produces $N_2(g)$ and $H_2O(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The ΔH°_f of $B_2H_6(g)$, $CH_4(g)$, and $N_2H_4(l)$ may be found in Appendix H.
Check answers: [28]
44. How much heat is produced when 1.25 g of chromium metal reacts with oxygen gas under standard conditions?
45. Ethylene, C_2H_2, a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst.
$$C_2H_4(g) + H_2O(g) \longrightarrow C_2H_5OH(l)$$
Using the data in the table in Appendix H, calculate $\Delta H°$ for the reaction.
Check answers: [29]
46. The oxidation of the sugar glucose, $C_6H_{12}O_6$, is described by the following equation:
$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H = -2816 \text{ kJ}$ The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.(a) How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?(b) How many Calories can be produced by the metabolism of 1.0 g of glucose?
47. Propane, C_3H_8, is a hydrocarbon that is commonly used as a fuel. (a) Write a balanced equation for the complete combustion of propane gas. (b) Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: we will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2 per litre.) (c) The heat of combustion of propane is −2,219.2 kJ/mol. Calculate the heat of formation, ΔH°_f of propane given that ΔH°_f of $H_2O(l)$ = −285.8 kJ/mol and ΔH°_f of $CO_2(g)$ = −393.5 kJ/mol. (d) Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.
Check answers: [30]
48. During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).

a. Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.
b. How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8: density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $CO_2(g)$ and $H_2O(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.
c. What mass of carbon dioxide is produced by combustion of the methane used to heat the house?
d. What mass of water is produced by combustion of the methane used to heat the house?
e. What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.
f. How many kilowatt–hours (1 kWh = 3.6×10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.
g. Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

Attribution & References

Except where otherwise noted, this section is adapted by JR van Haarlem from "1.3 Physical and Chemical Properties", "9.1 Energy Basics", "9.2 Calorimetry" and "9.3 Enthalpy" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* . / End of chapter exercises extracted from 1.3, 9.1, 9.2 and 9.3.

Notes

1. (a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical
2. physical
3. The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.
4. Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect "cancel" this dependence on amount, yielding a ratio that is

independent of amount (an intensive property).

5. The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.
6. Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.
7. (a) 47.6 J/°C; 11.38 cal °C−1; (b) 407 J/°C; 97.3 cal °C−1
8. 1310 J; 313 cal
9. 7.15 °C
10. (a) 0.390 J/g °C; (b) Copper is a likely candidate.
11. We assume that the density of water is 1.0 g/cm3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. Energy required = 7.47 kWh
12. lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser
13. greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings": qrxn = −(qsolution + qcalorimeter); since both qsolution and qcalorimeter are negative, including the latter term (qrxn) will yield a greater value for the heat of the dissolution
14. The temperature of the coffee will drop 1 degree.
15. 5.7 × 102 kJ
16. 38.5 °C
17. −2.2 kJ; The heat produced shows that the reaction is exothermic.
18. 1.4 kJ
19. 22.6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.
20. 11.7 kJ
21. 30%
22. 1.4 × 102 Calories
23. 79. −54.04 kJ mol−1
24. −2660 kJ mol−1
25. −66.4 kJ
26. −122.8 kJ
27. 3.7 kg
28. On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.
29. −88.2 kJ
30. (a) $C_3H_8(g)+5O_2(g)\rightarrow 3CO_2(g)+4H_2O(l)$; (b) 1570 L air; (c) −104.5 kJ mol^{-1}; (d) 75.4 °C

CHAPTER 5. INTRODUCTORY ATOMIC THEORY AND STRUCTURE

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- Dalton's atomic theory
- Basic concepts in electric charge

- The discoveries of an atom's subatomic particles atom including electrons, protons, and neutrons
- The structure of the nuclear atom and how neutral atoms form ions
- Isotopes of elements and how to read and write isotope symbols
- Atomic masses of elements and their isotopes and how to calculate percent abundance.

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- How to reference element names, symbols, and masses from the periodic table
- How to use your scientific calculator to perform percent calculations

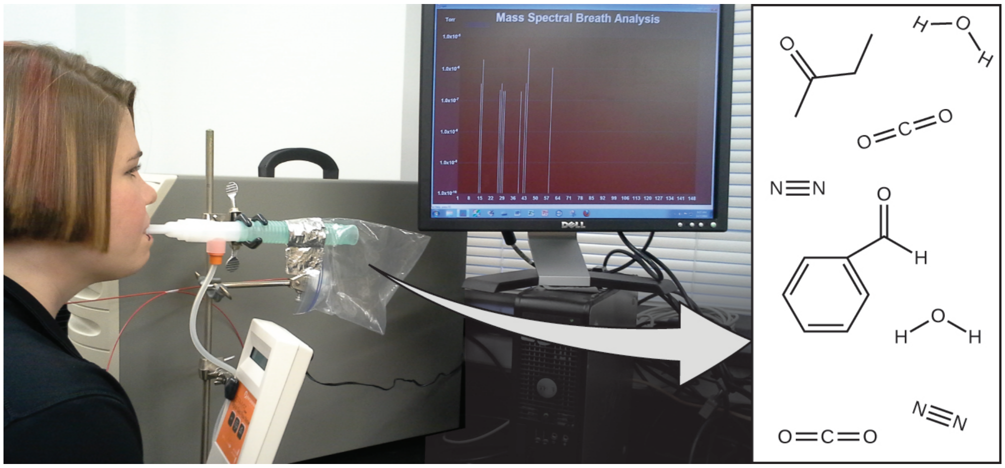

Figure 5a Mass Spectral Breath Analysis: Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers in *Chemistry (OpenStax)*, CC BY 4.0).

Your overall health and susceptibility to disease depends upon the complex interaction between your genetic makeup and environmental exposure, with the outcome difficult to predict. Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer. Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

Attribution & References

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5.1 EARLY ATOMIC THEORY: DALTON'S MODEL OF THE ATOM

Learning Objectives

By the end of this section, you will be able to:

- Summarize the postulates of Dalton's atomic theory
- Apply Dalton's atomic theory to explain the laws of definite and multiple proportions

The language used in chemistry is seen and heard in many disciplines, ranging from medicine to engineering to forensics to art. The language of chemistry includes its own vocabulary as well as its own form of shorthand. Chemical symbols are used to represent atoms and elements. Chemical formulas depict molecules as well as the composition of compounds. Chemical equations provide information about the quality and quantity of the changes associated with chemical reactions.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, the composition and mass of an atom, and the variability of the composition of isotopes.

Atomic Theory through the Nineteenth Century

Watch **The 2,400-year search for the atom – Theresa Doud (6 mins)**

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and “elements” as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behaviour of matter could be explained using an atomic theory. First published in 1807, many of Dalton’s hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of **Dalton’s atomic theory**.

1. Matter is composed of exceedingly small, indivisible particles called atoms. An **atom** is the smallest unit of an element that can participate in a chemical change.
2. An **element** consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure 5.1a). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties

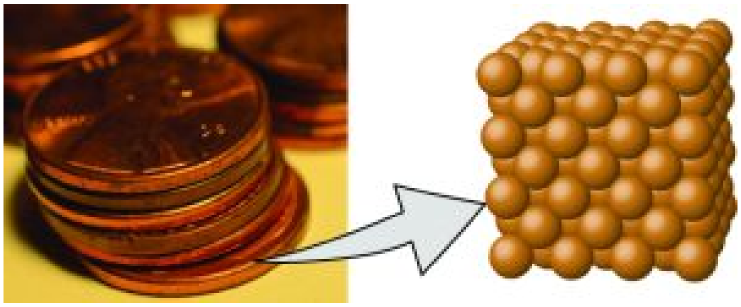


Figure 5.1a Macroscopic vs Microscopic Visual the Element Copper: A pre-1982 copper penny (left) contains approximately 3 × 10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by slgc, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure 5.1b).

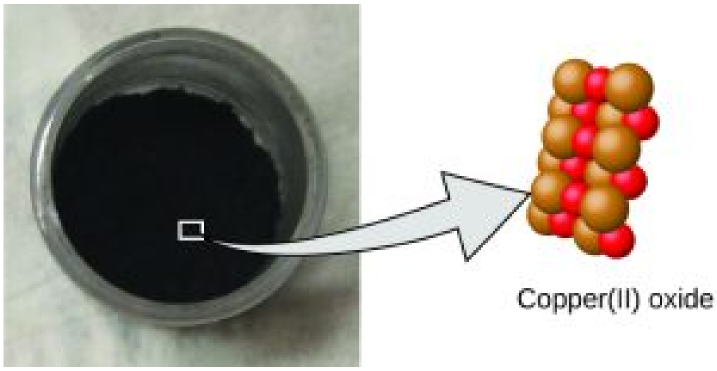


Figure 5.1b Macroscopic vs Microscopic Visual of the Compound Copper(II) Oxide: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown, larger spheres) and oxygen (red, smaller spheres)—in a 1:1 ratio. (credit: modification of work by Chemicalinterest, PD; in *Chemistry (OpenStax)*, CC BY 4.0).

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged and regrouped to yield substances that are different from those present before the change (Figure 5.1c).

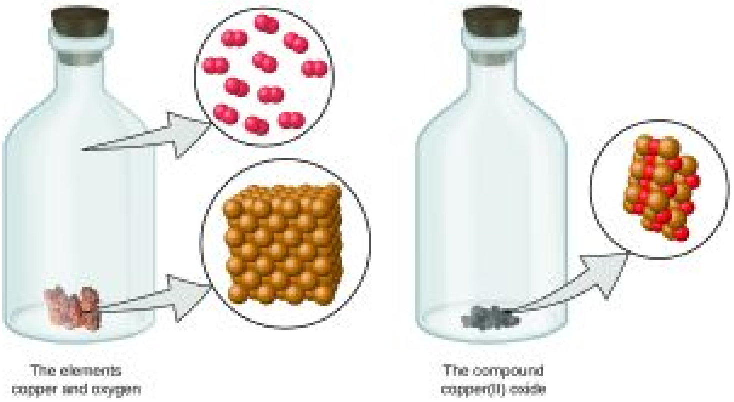


Figure 5.1c Visual of Dalton's Theory – Atoms are neither created nor destroyed during a chemical change but are rearranged to yield new substances. When the elements copper (a shiny, red-brown solid, shown here as brown spheres shaped as a cube) and oxygen (a clear and colourless gas, shown here as red spheres that are present in pairs) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by Anonymous, CC BY 3.0; in *Chemistry (OpenStax)*, CC BY 4.0).

Dalton's atomic theory laid the foundation in the development of chemistry. Most of his postulates remain valid; however, some of his conclusions have been revolutionized because further investigations have shown that

1. Atoms are composed of subatomic particles; they are not indivisible
2. Not all the atoms of a specific element have the exact same mass; an element can exist in different forms, called isotopes
3. Atoms, under special conditions, can be decomposed.

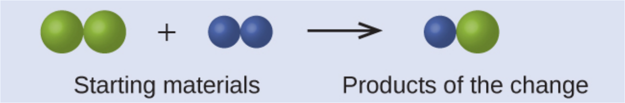
Source: (Hein & Arena, 2014, p. 83)

Despite these flaws, Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

Example 5.1a

Testing Dalton's Atomic Theory

In the following drawing, the green, larger spheres represent atoms of a certain element. The blue, smaller spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

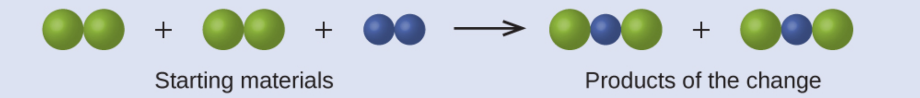


Solution

The starting materials consist of two green, larger spheres and two blue, smaller spheres. The products consist of only one green sphere and one blue sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

Exercise 5.1a

In the following drawing, the green, larger spheres represent atoms of a certain element. The blue, smaller spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



Check Your Answer

1

Exercise 5.1b

Check Your Learning Exercise (Text Version)
Choose the answer that best answers the questions for each of the multiple choice questions.

1. According to Dalton's Atomic Theory, matter consists of indivisible
   a. Molecules
   b. Cells
   c. Atoms
   d. Subatomic particles
2. Dalton's Atomic Theory postulates mass is neither created nor destroyed in a chemical reaction. This supports the
   a. Law of constant proportions
   b. Law of conservation of mass
   c. Law of multiple proportions
   d. Law of electric force

3. Fill in the blanks with the correct pair of terms from the choices below according to Dalton's Atomic Theory: All atoms of a given element have identical ________ including identical _______.
    a. Temperature, volume
    b. Force, pressure
    c. Weight, volume
    d. Physical and chemical properties, mass
4. Which of the following is NOT a postulate of Dalton's Atomic Theory?
    a. Atoms that combine to form new molecules do so in simple, whole number ratios
    b. A chemical reaction is a rearrangement of atoms. No atoms are created or destroyed.
    c. All elements are composed of small particles called atoms.
    d. Atoms of a given element are always identical.
    e. Atoms are always on motion
5. 5. Most of Dalton's postulates remain valid; however, some of Dalton's atomic theory postulates have been proven to be false. Which of the following postulates were determined to be incorrect?
    a. Matter is composed of exceedingly small, indivisible particles.
    b. Elements consist of only one type of identical atom, which has the same mass for all atoms.
    c. Theories stated in a) and b) were both proven to be false
    d. Neither theory stated in a) nor b) were proven to be false

Check Your Answer

2

Source: "Exercise 5.1b" by Jackie MacDonald, licensed under CC BY-NC-SA 4.0

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the **law of definite proportions** or the **law of constant composition**. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 5.1a.

Table 5.1a Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\text{g carbon}}{2.78\text{g hydrogen}} = \frac{5.33\text{g carbon}}{1.00\text{g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33\text{g carbon}}{4.19\text{g hydrogen}} = \frac{5.33\text{g carbon}}{1.00\text{g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40\text{g carbon}}{3.64\text{g hydrogen}} = \frac{5.33\text{g carbon}}{1.00\text{g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33 : 1.00.

Watch **Thinking Reeds Chemistry – The Law of Definite Proportions (4 mins 13 sec)**

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The **law of multiple proportions** states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

$$\frac{\frac{1.116\text{g Cl}}{1\text{g Cu}}}{\frac{0.558\text{g Cl}}{1\text{g Cu}}} = \frac{2}{1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound. When referencing Figure 5.1d, the above can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound (Figure 5.1d (b)) is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound (Figure 5.1d (a)) is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms in compound B compared to compound A (and thus the ratio of their masses) is therefore 2 to 1 (Figure 5.1d).

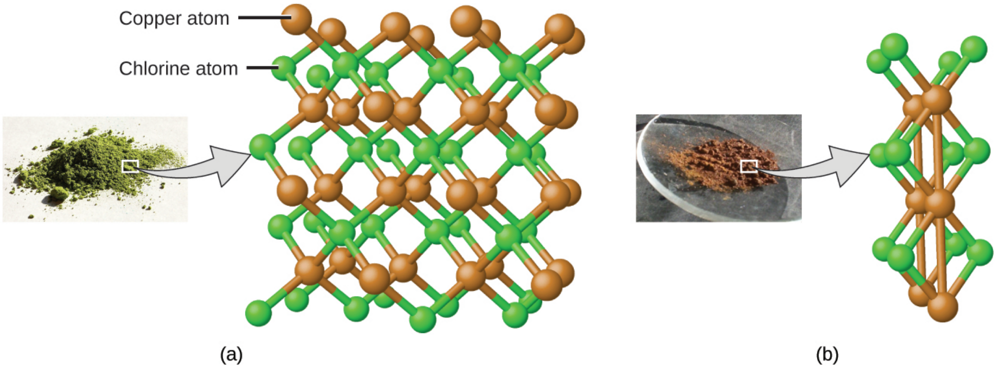


Figure 5.1d Law of Multiple Proportions: Comparing two different compounds containing variable amounts of copper and chlorine atoms. Compared to the copper chlorine compound in (a), where copper is represented by brown, larger spheres and chlorine by green, smaller spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by Benjah-bmm27, PD; credit b: modification of work by Walkerma, PD; in *Chemistry (OpenStax)*, CC BY 4.0).

Watch Multiple Proportions (1 min 11 sec)

Example 5.1b

Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colourless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colourless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of carbon to oxygen is:

$$\frac{1.33\text{g O}}{1\text{g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

$$\frac{2.67\text{g O}}{1\text{g C}}$$

The ratio of these ratios is:

$$\frac{\frac{1.33\text{g O}}{1\text{g C}}}{\frac{2.67\text{g O}}{1\text{g C}}} = \frac{1}{2}$$

The ratio of oxygen atoms of compound A to compound B (and thus the ratio of their masses) is 1 to 2. This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much oxygen per amount of carbon as compound B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO_2.

Exercise 5.1c

A sample of compound X (a clear, colourless, combustible liquid with a noticeable odour) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colourless, combustible liquid with a noticeable odour that is slightly different from X's odour) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Check Your Answer

3

Links to Interactive Learning Tools

Explore the Timeline of Atomic Discovery from eCampusOntario H5P Studio.

Attribution & References

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References

Hein, M., & Arena, S. (2014). *Foundations of College Chemistry (14th edition)*. Wiley & Sons.

Notes

1. The starting materials consist of four green, larger spheres and two blue, smaller spheres. The products consist of four green, larger spheres and two blue, smaller spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.
2. 1c; 2b; 3d; 4e; 5c
3. In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13\text{g C}}{2.96\text{g H}}$. In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91\text{g C}}{3.34\text{g H}}$. The ratio of these ratios is $\frac{\frac{14.13\text{g C}}{2.96\text{g H}}}{\frac{19.91\text{g C}}{3.34\text{g H}}} = \frac{4.77\text{g C/g H}}{5.96\text{g C/g H}} = 0.800 = \frac{4}{5}$. This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

5.2 ELECTRIC CHARGE

Learning Objectives

By the end of this section, you will be able to:

- Describe the concept of electric charge and its properties

In the two centuries since Dalton developed his ideas, scientists have made significant progress in advancing our understanding of atomic theory. Some of this development came from the results of several pioneering experiments that revealed details of electric charge and discovery of ions. Before you learn about the internal structure of an atom and the experiments that led to their discovery, it is important to outline key concepts in electric charge and about the discovery of ions.

Electric Charge

You are certainly familiar with electronic devices that you activate with the click of a switch, from computers to cell phones to television. And you have certainly seen electricity in a flash of lightning during a heavy thunderstorm. But you have also most likely experienced electrical effects in other ways, maybe without realizing that an electric force was involved. Let's take a look at some of these activities and see what we can learn from them about electric charges and forces.

Discoveries

You have probably experienced the phenomenon of **static electricity**: When you first take clothes out of a dryer, many (not all) of them tend to stick together; for some fabrics, they can be very difficult to separate. Another example occurs if you take a woolen sweater off quickly—you can feel (and hear) the static electricity pulling on your clothes, and perhaps even your hair. If you comb your hair on a dry day and then put the comb close to a thin stream of water coming out of a faucet, you will find that the water stream bends toward (is attracted to) the comb (Figure 5.2a).

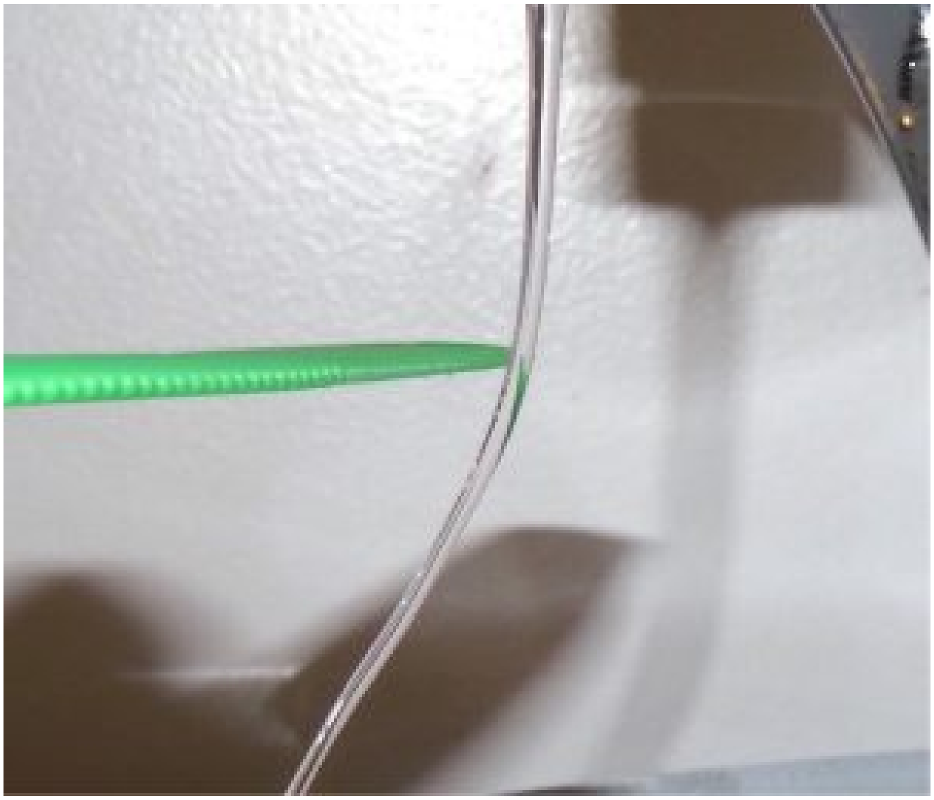

Figure 5.2a Electric Charge Real Life Example 1: An electrically charged comb attracts a stream of water from a distance. Note that the water is not touching the comb. (credit: Jane Whitney in *University Physics Volume 2 (Open Stax)*, CC BY 4.0).

Suppose you bring the comb close to some small strips of paper; the strips of paper are attracted to the comb and even cling to it (Figure 5.2b). In the kitchen, quickly pull a length of plastic cling wrap off the roll; it will tend to cling to most any nonmetallic material (such as plastic, glass, or food). If you rub a balloon on a wall for a few seconds, it will stick to the wall. Probably the most annoying effect of static electricity is getting shocked by a doorknob (or a friend) after shuffling your feet on some types of carpeting.

Figure 5.2b Electric Charge Real Life Example 2: After being used to comb hair, this comb attracts small strips of paper from a distance, without physical contact. Investigation of this behaviour helped lead to the concept of the electric force (credit: Jane Whitney in *University Physics Volume 2 (Open Stax)*, CC BY 4.0).

Many of these phenomena have been known for centuries. The ancient Greek philosopher Thales of Miletus (624–546 BCE) recorded that when amber (a hard, translucent, fossilized resin from extinct trees) was vigorously rubbed with a piece of fur, a force was created that caused the fur and the amber to be attracted to each other. Additionally, he found that the rubbed amber (Figure 5.2c) would not only attract the fur, and the fur attract the amber, but they both could affect other (nonmetallic) objects, even if not in contact with those objects. (Figure 5.9)

Figure 5.2c Image of Borneo Amber: Borneo amber is mined in Sabah, Malaysia, from shale-sandstone-mudstone veins. When a piece of amber is rubbed with a piece of fur, the amber gains more negative charge, giving it a net negative charge. At the same time, the fur, having lost what we now know to be called electrons, becomes positively charged. (credit: work by Sebakoamber, PD)

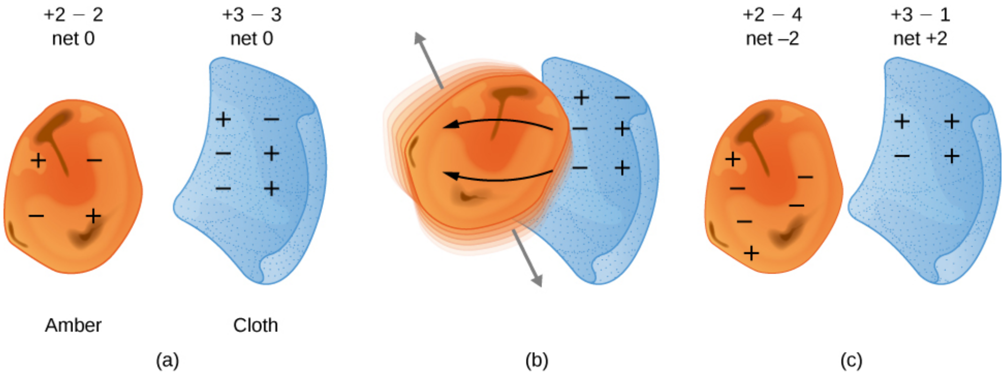

Figure 5.2d Visual of Attractive Forces: When materials are rubbed together, charges can be separated, particularly if one material has a greater affinity for electrons than another. (a) Both the amber and cloth are originally neutral, with equal positive and negative charges. Only a tiny fraction of the charges are involved, and only a few of them are shown here. (b) When rubbed together, some negative charge is transferred to the amber, leaving the cloth with a net positive charge. (c) When separated, the amber and cloth now have net charges, but the absolute value of the net positive and negative charges will be equal (credit: *University Physics Volume 2 (Open Stax)*, CC BY 4.0).

The English physicist William Gilbert (1544–1603) also studied this attractive force, using various substances. He worked with amber, and, in addition, he experimented with rock crystal and various precious and semi-precious gemstones. He also experimented with several metals. He found that the metals never exhibited this force, whereas the minerals did. Moreover, although an electrified amber rod would attract a piece of fur, it would repel another electrified amber rod; similarly, two electrified pieces of fur would repel each other.

This suggested there were two types of an electric property, which eventually came to be called **electric charge**. It was concluded there were two types of electric charge – positive and negative. The difference between the two types of electric charge is in the directions of the **electric forces** that each type of charge causes:

- These forces are repulsive when the same type of charge exists on two interacting objects
- These forces are attractive when the charges are of opposite types

The most peculiar aspect of this new force is that it does not require physical contact between the two objects in order to cause an acceleration. This is an example of a so-called "long-range" force, (or, as James Clerk Maxwell later phrased it, "action at a distance"), which later became known as a form of induction.

The properties of electric charge are as follows:

- Charges can be positive and negative
- Electric force can be either attractive or repulsive
  - If two interacting objects carry the same sign of charge, the force is repulsive.
    - This interaction is referred to as **electrostatic repulsion**
  - If the charges are of opposite sign, the force is attractive.
    - This interaction is referred to as **electrostatic attraction**
- The magnitude of the force decreases (rapidly) with increasing separation distance between objects. The magnitude of the force increases (rapidly) with decreasing separation distance between the objects.
- The force acts by contact or induction (without physical contact between the two objects)
- Not all objects are affected by this force

Exercise 5.2a

Check Your Learning Exercise (Text Version)
Read the following statement about electric charge and determine whether the statement is True OR False.

1. Charges can be positive and neutral
2. Electric force can be either attractive or equal
3. If two interacting objects carry the same sign of charge, it results in electrostatic repulsion

4. If the charges are of opposite sign, the force is attractive.
5. If a balloon is rubbed on hair to gain charge and then is placed against a wall and sticks to the wall, the two objects have opposite charges
6. The magnitude of the force decreases (rapidly) with decreasing separation distance between objects
7. When two objects of similar charge repel each other without contact it is called induction.
8. All objects are affected by electric force

Check Your Answer[1]

Source: "Exercise 5.2a" by Jackie MacDonald, licensed under CC BY-NC-SA 4.0

The discovery that matter (and its atoms) has properties of electric charge and contain both positive and negative charges led to the theory that a given neutral atom may be able to lose or gain such charges and become positively or negatively charged atoms, respectively. These charged atoms were later defined as positive ions – cations and negative ions – anions. This concept will be discussed in more detail in upcoming sections and chapters.

Attribution & References

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Notes

1. For the following answers, any false answers, have been rewritten to show the correct statement. The bolded words (also noted with an *) were changed from the original false statement to make the statement true.
   1. False - Charges can be positive and ***negative**;
   2. False - Electric force can be either attractive or ***repulsive**;
   3. True;
   4. True;
   5. True;
   6. False - The magnitude of the force decreases (rapidly) with ***increasing** separation distance between objects OR The magnitude of the force ***increases** (rapidly) with decreasing separation distance between objects;

7. True;
8. False – *****Not** all objects are affected by electric force

5.3 SUBATOMIC PARTICLES OF THE ATOM

Learning Objectives

By the end of this section, you will be able to:

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms

Scientists have made significant progress in furthering our understanding of atomic theory. Much of this came from the results of several seminal experiments that revealed the details of the internal structure of atoms. Here, we will discuss some of those key developments, with an emphasis on the application of the scientific method, as well as understanding how the experimental evidence was analyzed. While the historical persons and dates behind these experiments can be quite interesting, it is most important to understand the concepts resulting from their work.

Atomic Theory after the Nineteenth Century

If the matter were composed of atoms, what were atoms composed of? Was it just predominately European scientists questioning the properties of matter, its constituents, its behaviour, and why and how it exists? Or at that time, were other groups of people around the world, such as Indigenous communities, also asking similar questions? From their experiences, traditions, and cultural practices did they test their own hypotheses about the different matter around them – what makes mud, mud, and why is it different from sweetgrass before and after it is burned? Did they, too, ask the question what makes the smallest particles, or is there something smaller? The matter is made up of inconceivably small atoms, and yet scientists found atoms contain even smaller subatomic particles, including electrons, protons, and neutrons. The discovery of these subatomic particles is discussed next.

Revelation of the Electron

In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made in 1897 by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure 5.3a).

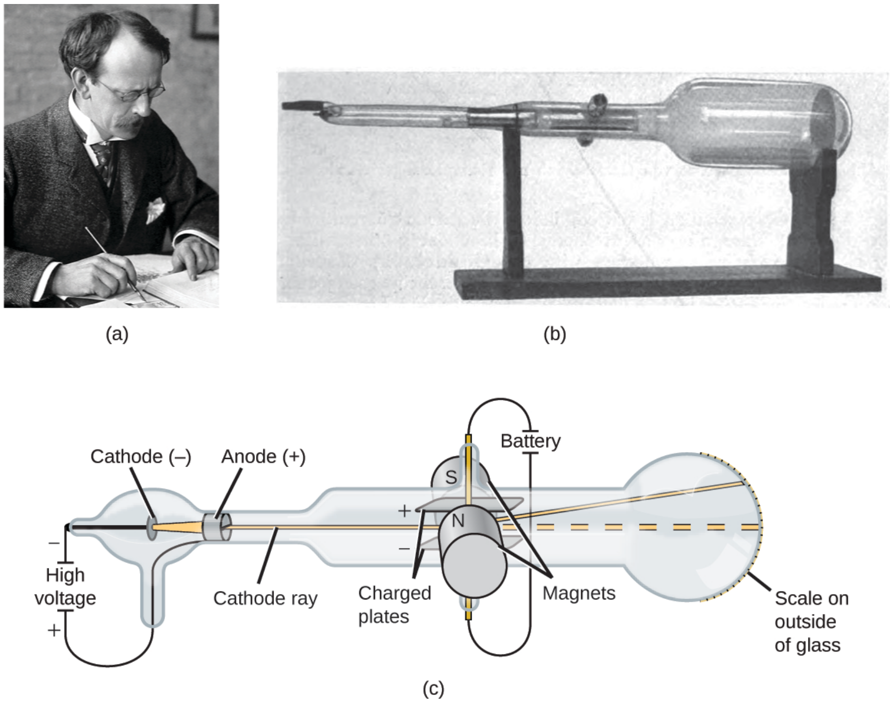


Figure 5.3a Thomson Cathode Ray Experiments: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation, PD; credit b: modification of work by Eugen Nesper, PD; credit c: modification of work by Kurzon, PD).

Based on his observations, here is what Thomson proposed and why:

- The particles are attracted by positive (+) charges and repelled by negative (−) charges, so the particles of

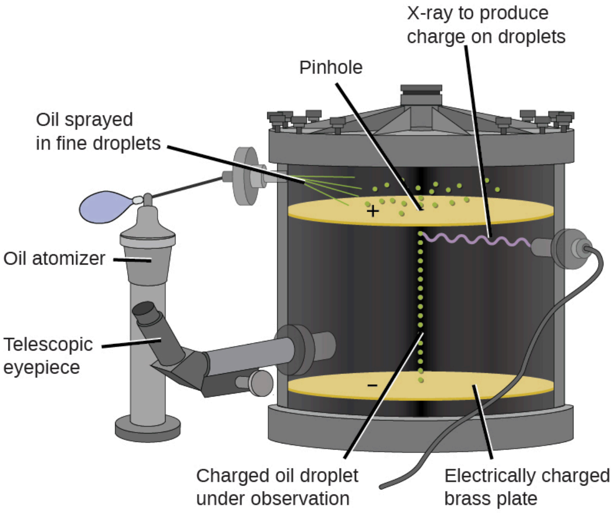
the cathode ray must be negatively charged since like charges repel and unlike charges attract.
- they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms.

Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an **electron**, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term "electron" was initially coined in 1891 by Irish physicist George Stoney, meaning "electric ion." Stoney originally recognized the atom must have a unit of electricity and charge associated with the atom, but he had no experimental proof. It was J.J Thomson who took this theory and orchestrated scientific experiments using the cathode rays to prove atoms contained charged particles – the fundamental unit of charge – the electron.

J.J. Thomson Talks About the Size of the Electron

Listen to Thomson describe his discovery in his own voice.

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 5.3b).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure 5.3b Millikan's Oil Drop Experiment: Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. The symbol C – the coulomb – is the unit of electric charge in the International System of Units (SI). Millikan concluded that this electric charge value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

$$\text{Mass of electron} = 1.602 \times 10^{-19}\text{C} \times \frac{1\text{kg}}{1.759 \times 10^{11}\text{C}} = 9.107 \times 10^{-31}\text{kg}$$

A summary of the important concepts discovered about electrons include:

- They are negatively charged subatomic particles
- Mass of the electron is found to be 9.110×10^{-28} g or 9.110×10^{-31} kg
- The charge on the electron is -1.602×10^{-19} coulombs
    - when considering the chemical behaviour of subatomic particles in an atom and its ability to form ions, it is customary to consider these particles as having a relative charge: An electron carries a negative charge (-1) and is represented by the symbol, e^-.

Scientists had now established that the atom was not indivisible as Dalton had believed, but consisted of smaller subatomic charged particles. Due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. It is suggested that the proton was observed by Eugen Goldstein in 1886 when he used anode rays of a hydrogen ion. However, it was the later experiments of J.J. Thomson and Ernest Rutherford that uncovered the nature of the positively charged proton. In 1904, Thomson proposed the "plum pudding" model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure 5.3c)

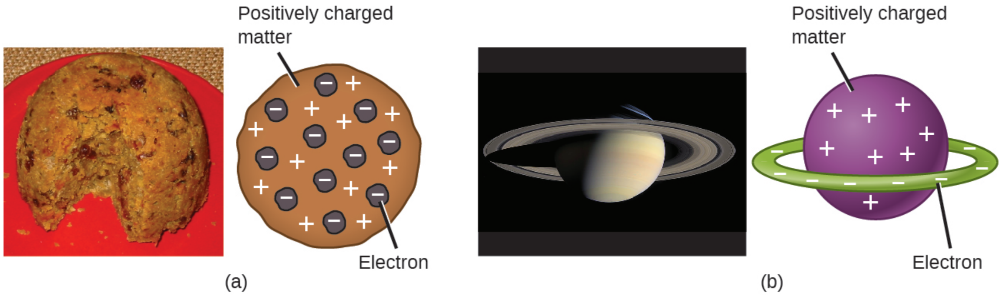


Figure 5.3c Early Models of the Atom and its Subatomic Parts. (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by Man vyi, PD; credit b: modification of work courtesy of NASA/JPL-Caltech, JPL Image Policy; in *Chemistry (OpenStax)*, CC BY 4.0).

Revelation of the Proton

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged **alpha particles (α particles)** that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay if you study nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 5.3d). Rutherford described finding these results: “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you” [1]

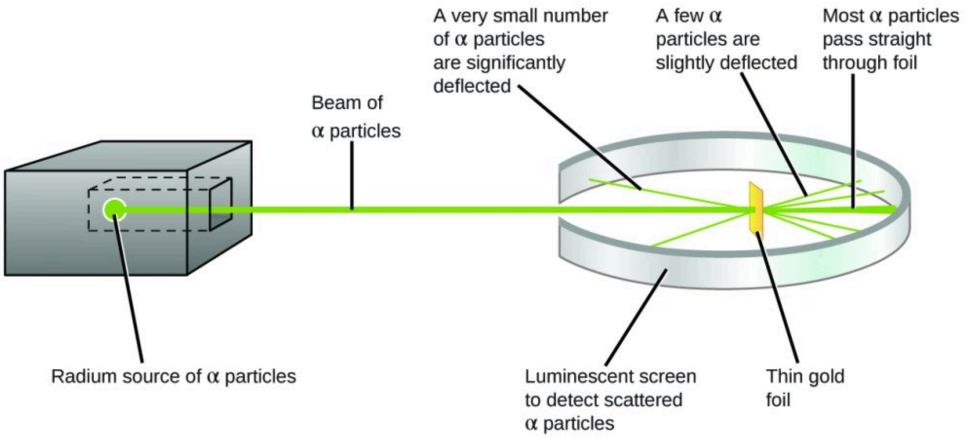


Figure 5.3d Rutherford Gold Foil Experiment Schematic: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge. Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, termed the **nucleus**, must be at the centre of each atom.

The Rutherford Experiment

This simulation of the Rutherford gold foil experiment allows you to adjust the slit width to produce a narrower or broader beam of α particles to see how that affects the scattering pattern.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure 5.3e). After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a “building block,” and he named this more fundamental particle the **proton**, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

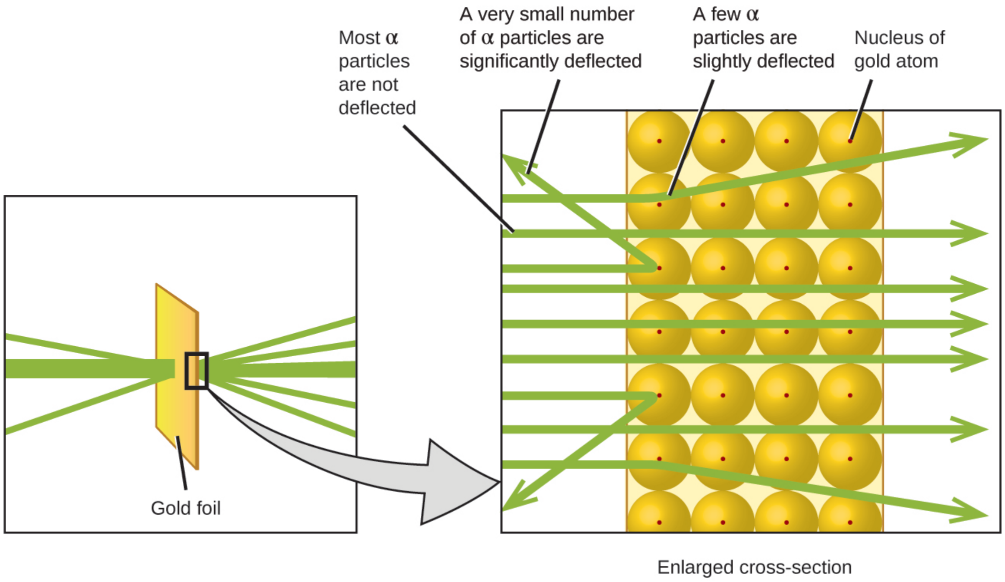


Figure 5.3e Rutherford Gold Foil Experiment – Microscopic Visual. The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 5.3a

Investigate the differences between a "plum pudding" atom and a Rutherford atom by firing α particles at each type of atom using the following PhET simulation: Rutherford Scattering

A summary of the important concepts discovered about protons include:

- Protons are positively charged subatomic particles
- Mass of the proton is found to be 1.673 x 10^{-24} g, which is 1,836 times the mass of an electron.
- Protons are found in the central part of an atom called the nucleus.
- The charge on the proton is +1.602 x 10^{-19} coulombs

  - When considering the chemical behaviour of subatomic particles in an atom and its ability to form ions, it is customary to consider these particles as having a relative charge: A proton carries a positive charge (+1) and is represented by the symbol p^+. As noted earlier, an electron carries a negative charge (-1) and is represented by the symbol, e^-. In a neutral atom, the number of protons equals the number of electrons, which means atoms of a given element are neutral.

The Neutron

One puzzle remained with regard to the subatomic particles of an atom. The nucleus of an atom was known to contain almost all of the mass of an atom, but the number of protons was only providing half, or less, of that atom's mass. Therefore, there must be some other type of subatomic matter present in the nucleus that had yet to be discovered. Different proposals were made to explain what constituted the remaining mass, while still maintaining the neutral charge of the atom – the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of **neutrons**, uncharged, subatomic particles with a mass approximately the same as that of protons, 1.67493×10^{-24} g. Neutrons, having no relative electric charge and are represented by the symbol n^0. The existence of the neutron also explained isotopes, alternative forms of a given element. Isotopes of a given element differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. The concept of isotopes will be explained in more detail later in this chapter.

Watch The Subatomic Particles (3 mins 11 s)

Exercise 5.3b

Check Your Learning Exercise (Text Version)
Review the scientist name list below. Match each of the seven scientists with their key discovery by filling in the [BLANK] with the correct scientist's name.

Scientist Name List (includes 7 names):

Democritus, Aristotle, John Dalton, J.J Thomson, Robert Millikan, Ernst Rutherford, James Chadwick

QUESTIONS:

1. The scientist who concluded that matter is composed of tiny, indivisible atoms that combine, separate, and rearrange in whole number ratios to form new matter is [BLANK].
2. [BLANK] is the scientist who postulated the nuclear model of the atom; the nuclear atom is

mostly empty space with nearly all of its mass concentrated in the tiny central positively charged nucleus, which is surrounded by negatively charged electrons.

3. The scientist who hypothesized that all matter was composed of small, finite particles that they called atomos, meaning "indivisible" is [BLANK].
4. [BLANK] identified the mass of an electron to be 9.109×10^-31 kilograms
5. [BLANK] suggested a philosophical concept of matter such that it consisted of four elements – fire, earth, air, and water – and could be infinitely divided
6. This scientist, [BLANK], discovered the neutron, a subatomic particle with no charge and is in the tiny nucleus of an atom.
7. [BLANK] performed experiments with cathode ray tubes and discovered that all atoms contain tiny negatively charged subatomic particles and called them electrons. This scientist proposed the plum pudding model of the atom, which had a uniform sphere of positive charge with negatively charged electrons embedded within the sphere.

Check Your Answer[2]

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Notes

1. Ernest Rutherford, "The Development of the Theory of Atomic Structure," ed. J. A. Ratcliffe, in Background to Modern Science, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/items/backgroundtomode032734mbp/backgroundtomode032734mbp.pdf. (p. 68).
2. (1) John Dalton; (2) Ernst Rutherford; (3) Democritus; (4) Robert Millikan; (5) Aristotle; (6) James Chadwick; (7) J.J Thomson

5.4 DEFINING THE NUCLEAR ATOM

Learning Objectives

By the end of this section, you will be able to:

- Summarize the structural characteristics of the nuclear atom
- Illustrate a simple model of the nuclear atom; locate its subatomic particles and their charges
- Explain why atoms have no overall charge
- Define ion and use the number of electrons lost or gained from an atom to calculate the overall charge of the ion and write the corresponding ion symbol.

The idea that matter is composed of tiny particles called atoms is at least 25 centuries old. It took until the twentieth century, however, for scientists to invent instruments that permitted them to probe inside an atom and find that it is not, as had been thought, hard and indivisible as Dalton theorized. Instead, experiments by Thomson, Rutherford, Chadwick, and other scientists revealed the atom is a complex structure composed of still smaller subatomic particles – electrons, protons, and neutrons.

Probing the Nuclear Atom

You have learned in the previous section that the first of these smaller particles were discovered by British physicist James (J. J.) Thomson in 1897. Named the *electron*, this particle is negatively charged. (It is the flow of these particles that produces currents of electricity, whether in lightning bolts or in the wires leading to your lamp.) Because an atom in its normal state is electrically neutral, each electron in an atom must be balanced by the same amount of positive charge.

The next step was to determine where in the atom the positive and negative charges were located. British physicist Ernest Rutherford devised the alpha-particle scattering, gold foil experiment that provided part of the answer to this question. The only way to account for the alpha particles that reversed direction when they hit the gold foil was to assume that nearly all of the mass, as well as all of the positive charge in each individual gold atom, is concentrated in a tiny centre or nucleus. When a positively charged alpha particle strikes a nucleus, it reverses direction, much as a cue ball reverses direction when it strikes another billiard ball. He termed this positive charge – a proton. Rutherford's model also placed the other type of charge—the negative electrons—in orbit around this nucleus.

Rutherford's model required that the electrons be in motion. Positive and negative charges attract each other, so stationary electrons would fall into the positive nucleus. Also, because both the electrons and the nucleus are extremely small, most of the atom is empty, which is why nearly all of Rutherford's particles were able to pass right through the gold foil without colliding with anything. Rutherford's model was a very successful explanation of the experiments he conducted, although eventually, scientists would discover that even the nucleus itself has structure.

Chadwick identified the neutron (n^0). It has neither a positive nor a negative charge, so it is considered neutral. It was determined that neutrons are also located in the nucleus (centre) of the atom with protons, and like protons, have a similar mass.

Collectively, these experimental observations, especially Rutherford's experiments, provided insight into the structure of the nuclear atom. The majority of the atom's structure is made up of empty space, with a centrally located, very concentrated nucleus. The nucleus contains positively charged protons and neutrally charged neutrons. Combined, these account for the majority of the mass in a given atom. The negative electrons, which contribute very little to the overall mass of the atom, are in orbit around the nucleus within the empty space.

The simplest possible atom (and the most common one in the sun and stars) is the element hydrogen (H). The nucleus of ordinary hydrogen contains a single proton. Moving around this proton is a single electron. Recall, the mass of an electron is nearly 2000 times smaller than the mass of a proton, and the electron carries an amount of charge exactly equal to that of the proton but opposite in sign (Figure 5.4a). Opposite charges attract each other, so it is an electromagnetic force that holds the proton and electron together. But what about the neutron(s)? The diagram below does not show hydrogen with any neutrons. In fact, hydrogen (the first element on the periodic table) has only one proton in the nucleus and one orbiting electron but does not contain any neutrons. Hydrogen actually has 3 naturally occurring forms that are all a little bit different from one another. The one shown below is the most abundant form of hydrogen in nature. These different forms of the same element are called **isotopes**. The concept of isotopes will be discussed in this section and in greater detail later in this chapter.

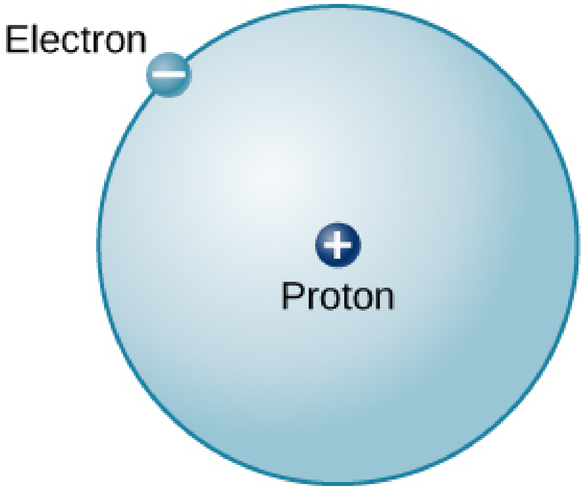

Figure 5.4a Hydrogen-1 Atom: This is a schematic diagram of a hydrogen atom. The proton and electron have equal but opposite charges, which exert an electromagnetic force that binds the hydrogen atom together. In the illustration, the size of the particles is exaggerated so that you can see them; they are not to scale. They are also shown much closer than they would actually be as it would take more than an entire page to show their actual distance to scale (credit: *Astronomy 2e (Open Stax)*, CC BY 4.0).

There are many other types of atoms in nature. Helium, for example, is the second-most abundant element in the Sun. Helium has two protons in its nucleus instead of the single proton that characterizes hydrogen. In addition, the helium nucleus contains two neutrons, particles with a mass comparable to that of the proton but with no electric charge. Moving around this nucleus are two electrons, so the total net charge of the helium atom is also zero (Figure 5.4b).

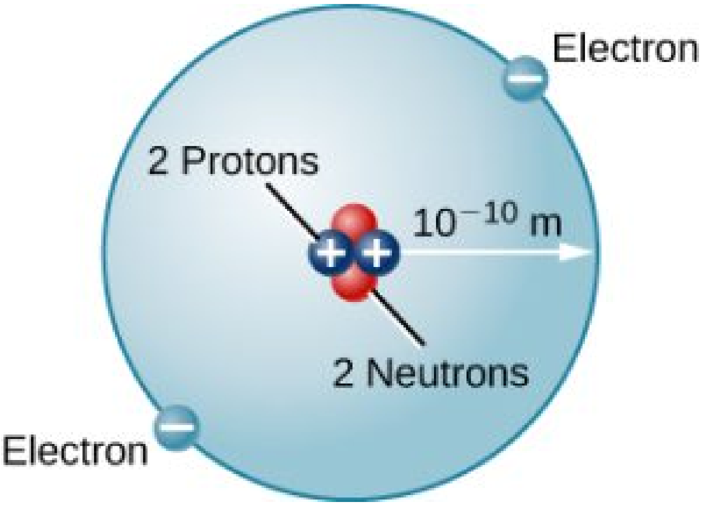

Figure 5.4b Helium Atom. Here we see a schematic diagram of a helium atom in its lowest energy state. Two protons are present in the nucleus of all helium atoms. In the most common variety of helium, the nucleus also contains two neutrons, which have nearly the same mass as the proton but carry no charge. Two electrons orbit the nucleus (credit: *Astronomy 2e (Open Stax)*, CC BY 4.0).

From this description of hydrogen and helium, perhaps you have guessed the pattern for building up all the elements (different types of atoms) that we find in the universe. The type of element is determined by the number of protons in the nucleus of the atom. Every element has a specific atomic number that equals the number of protons it contains; an element's atomic number can be sourced from the periodic table. For example, any atom with six protons is the element carbon, with eight protons is oxygen, with 26 is iron, and with 92 is uranium. On Earth, a typical atom has the same number of electrons as protons, and these electrons follow complex orbital patterns around the nucleus (which will be covered in more detail in chapter 10 – modern atomic theory).

Next, another model of the nuclear atom is shown in Figure 5.4c.

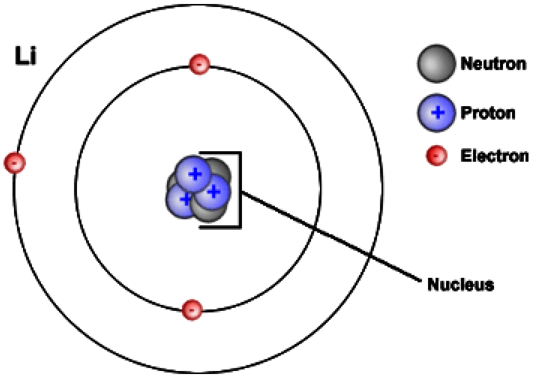

Figure 5.4c Diagram of the Atom: Atoms contain protons (+) and neutrons, which are found in the nucleus (centre) of the atom. Atoms also contain electrons (-), which are found outside the nucleus. This is a model of a lithium atom. (credit: “Diagram of an Atom” from *Introduction to Biology* by Open Learning Initiative is licensed under CC BY-NC-SA 3.0).

Formation of Ions

The number of protons, neutrons, and electrons an atom contains differentiates one type of atom from the next. In any given atom of an element when the number of positively charged protons and the number of negatively charged electrons are the same, the atom is neutral. Interestingly, an atom can lose or gain electrons – this is what gives an element its chemical properties, including its ability to combine with other elements to form new matter. When an atom has more or less electrons than protons, it is electrically charged and is called an **ion**. Recall that the relative charge of one proton is +1 and one electron is -1. The amount of charge is dependent on the number of electrons lost or gained. Ions have symbols and are written using the atomic symbol, with its quantity of charge and charge sign (+ or -) in superscript. Note for any atoms having a +1 or -1 charge, the 1 is omitted when writing the ion symbol.

The charge of an atom is determined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail later in this book, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an **anion**. Positively charged atoms called **cations** are formed when an atom loses one or more electrons. For example, a neutral sodium atom (atomic number = 11) has 11 protons and 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 – 10 = 1+); its ion symbol is Na^+. A neutral oxygen atom (atomic number = 8) has eight protons and 8 electrons, and if it gains two electrons it will become an anion with a 2– charge (8 – 10 = 2–); its ion symbol is O^{2-}.

In summary (also refer to Table 5.4a):

- Atoms that lose electrons will have less electrons than protons and form positive ions called cations.
- Atoms that gain electrons will have more electrons than protons and form negative ions called anions.

Table 5.4a Summarizing Ion formation and Terminology

Starting Atom	Gain / Lose Electrons	More / Less Electrons than Protons	Type of Ion	Ion Classification	Determining Charge
Neutral Atom	loses electron(s)	LESS e^-s	forms positive ion	cation	= # electrons lost to form ion
Neutral Atom	gains electron(s)	MORE e^-s	forms negative ion	anion	= # electrons gained to form ion

Source: "Table 5.4a" by Jackie MacDonald is licensed under CC BY-NC-SA 4.0.

Example 5.4a

Determining Ionic Symbols by Calculating Ionic Charge

A neutral lithium atom has 3 electrons and 3 protons. Determine the electric charge and write the ionic symbol for a lithium cation containing 2 electrons.

Solution

Lithium forms a CATION, a positive ion: The lithium ion has two electrons (2 e^-) and three protons (3 p^+), which means the neutral atom lost one electron (1 e^-).

CHARGE of Li ion = protons – electrons = 3 – 2 = +1; therefore, the ion has a net charge of +1.

ION SYMBOL for the lithium ion is Li^+

Example 5.4b

Determining Ionic Symbols by Calculating Ionic Charge

A neutral sulfur atom has 16 electrons and 16 protons. Determine the electric charge and write the ionic symbol for an sulfur anion containing 18 electrons.

Solution

Sulfur forms an ANION, a negative ion: The Sulfur ion has 18 electrons (18 e^{-}) and 16 protons (16 p^{+}), which means the neutral atom gained two electron (2 e^{-}).

CHARGE of S ion = protons – electrons = 16 – 18 = -2; therefore, the ion has an net charge of -2.

ION SYMBOL for the sulfur ion is S^{2-}

Example 5.4c

Determining Ionic Symbols by Calculating Ionic Charge

A neutral chlorine atom has 17 protons and 17 electrons. It gains one electron to form a chloride ion.

- Determine the electric charge on the ion and write the ionic symbol.
- Is the ion considered a cation or anion?
- How many total electrons does the chloride ion have?

Solution

A neutral chlorine atom gains one electron, so it will have a 1- charge; its symbol is Cl^{-}. Chlorine formed a negative ion, and is classified as an anion. Chloride ion has 18 electrons total (17 e^{-} + 1 e^{-} = 18 e^{-})

Exercise 5.4a

Check Your Learning Exercise (Text Version)
From the options provided in brackets for each statement, decide which of the provided choices is correct.

1. Arsenic as a neutral atom contains 33 protons and (32 / 33 / 36) electrons. As an ion it can have 36 electrons. The charge on this ion would be (3^{+} / 3^{-}). This type of ion is a(n) (cation / anion). The ion symbol for the ion is (As^{3+} / As^{3-}).

2. Barium as a neutral atom contains 56 protons and (54 / 56 / 58) electrons. As an ion it has 54 electrons. The charge on this ion would be (2^+ / 1^+ / 1^- / 2^-). This type of ion is a(n) (cation / anion). The ion symbol for the ion is (Ba^{2+} / Ba^{2-}).
3. Potassium as a neutral atom contains 19 protons and (18 / 19 / 20) electrons. Potassium loses one electron to form a(n) (cation / anion) that has a (1^- / 1^+) charge. This ion will have total of (18 / 19 / 20) electrons. The ion symbol for the ion is (K^+ / P^+ / K^- / P^-).

Check Your Answer[1]

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You will learn more about elements forming ions when reviewing concepts in chemical nomenclature, chemical reactions, and chemical bonding.

The Atomic Nucleus

The ratio of neutrons to protons increases as the number of protons increases, but each element is unique. The number of neutrons is not necessarily the same for all atoms of a given element. As aforementioned, most hydrogen atoms contain no neutrons at all. There are, however, hydrogen atoms that contain one proton and one neutron, and others that contain one proton and two neutrons. The various types of hydrogen nuclei with different numbers of neutrons are called isotopes of hydrogen (Figure 5.4d), and all other elements have isotopes as well. You can think of isotopes as siblings in the same element "family"—closely related but with different characteristics and behaviours. Turns out the element Hydrogen has three different isotopic forms, all containing one proton and one electron: Hydrogen – 1; Hydrogen – 2; and Hydrogen – 3, having 0, 1, and 2 neutrons in their atom nucleus, respectively. Hydrogen – 1 is the most abundant of the hydrogen isotopes and accounts for 99.9885% of all Hydrogen found in nature.

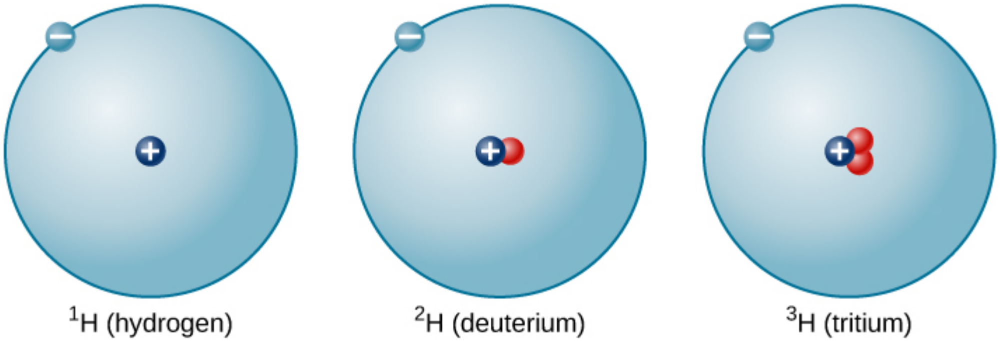

Figure 5.4d Isotopes of Hydrogen: A single proton in the nucleus defines the atom to be hydrogen, but there may be zero, one, or two neutrons. The most common isotope of hydrogen is the one with only a single proton and no neutrons (credit: *Astronomy 2e (Open Stax)*, CC BY 4.0).

Exercise 5.4b

Check Your Learning Exercise (Text Version)
Review the word list provided and choose a word or phase in the (BLANK) to make the statements correct. Each word will be used once.

WORD LIST: (11 words/phrases)

atomic number, protons, positively, electrons, neutron, isotopes, mass, empty space, ions, cations, anions

1. The nuclear model of the atom is made up of mostly (BLANK).
2. The atomic number tells you how many (BLANK) (and electrons) there are in a neutral atom.
3. The whole number found on the periodic table near an element symbol is called the (BLANK). It is unique for each element.
4. An atom with the same number of protons but different number of neutrons are called (BLANK).
5. The subatomic particle that has no charge is called a (BLANK).
6. The nucleus of the atom is (BLANK) charged. It contains protons and neutrons, which are the main subatomic particles that contribute to the overall (BLANK) of the atom.
7. Atoms can gain or lose (BLANK) to form positive or negative (BLANK).
8. A positive ion is called a(n) (BLANK); a negative ion is called a(n) (BLANK).

Check Your Answer[2]

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Exercise 5.4c

Practice using the following PhET simulation: Build an Atom

Links to Interactive Learning Tools

Explore Subatomic Particles from the Physics Classroom.

Explore Subatomic Particle Terminology from eCampusOntario H5P Studio.

Attribution & References

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Notes

1. (1) Arsenic as a neutral atom contains 33 protons and 33 electrons. As an ion it can have 36 electrons. The charge on this ion would be 3^-. This type of ion is a(n) anion. The ion symbol for the ion is As^{3-}. (2) Barium as a neutral atom contains 56 protons and 56 electrons. As an ion it has 50 electrons. The charge on this ion would be 2^+. This type of ion is cation. The ion symbol for the ion is Ba^{2+}. (3) Potassium as a neutral atom contains 19 protons and 19 electrons. Potassium loses one electron to form cation that has a 1^+ charge. This ion will have total of 18 electrons. The ion symbol for the ion is K^+.
2. (1) empty space; (2) protons; (3) atomic number; (4) isotopes; (5) neutron; (6) positively, mass; (7) electrons, ions; (8) cation, anion

5.5 ISOTOPES OF THE ELEMENTS

Learning Objectives

By the end of this section, you will be able to:

- Define isotopes and identify examples of isotopes for several elements
- Write and interpret symbols that depict the atomic number, mass number of isotopes
- Write isotope names using common naming methods

What is an Isotope?

Isotopes are various forms of the same element that have the same number of protons but a different number of neutrons. As the number of neutrons of an atom changes, so does its relative isotopic mass. The relative isotopic mass (also called mass number) is the sum of the protons and neutrons present in that isotope.

Mass Number (A) = Number of Protons + Number of Neutrons

Isotope symbols for elements are used to represent specific isotopes of atoms and include **mass number (A)** in superscript, **atomic number (Z)** in subscript, followed by the element symbol (X) in normal case (Figure 5.5a).

The number of protons in the nucleus of an atom is its atomic number (Z). This is the defining trait of an element. Its atomic number (Z) determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. If you change the atomic number to 7, you are no longer dealing with carbon atoms, but nitrogen atoms. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A). The number of neutrons in that atom is therefore the difference between the mass number (A) and the atomic number (Z).

In summary:

$$\begin{array}{rl} \text{atomic number (Z)} & \text{number of protons} \\ \text{mass number (A)} & \text{number of protons} + \text{number of neutrons} \\ \text{A - Z} & \text{number of neutrons} \end{array}$$

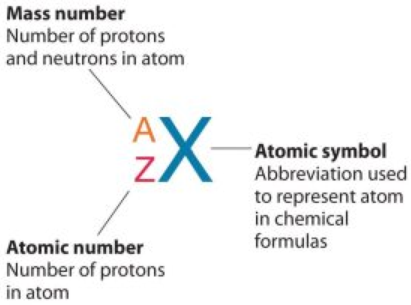

Figure 5.5a Isotope Symbols of Elements: A symbol template is used to differentiate one isotope from another. The element symbol is written to identify the element. A represents the isotope's mass number and symbol Z represents the isotope's atomic number. All isotopes of an element have the same number of protons and electrons, which means they exhibit similar chemical properties. (credit**:** "1.6 Isotopes and Atomic Masses" In *Principles of General Chemistry (v. 1.0)* by Anonymous, CC BY-NC-SA 3.0./ Adapted by Jackie MacDonald.

Examples of Isotopes and their Properties:

As mentioned above, the symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol. The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity (atomic number), as does its symbol, it is sometimes omitted, as shown in Figure 5.5b. The various isotopes for the element carbon and the number of each subatomic particle in that isotope are shown below:

- Carbon-12 (or ^{12}C) has the atomic number 6 and mass number 12 (six protons and six neutrons). It contains six protons, six neutrons, and six electrons
- Carbon-13 (or ^{13}C) has the atomic number 6 and mass number 13 (six protons and seven neutrons). It contains six protons, seven neutrons, and six electrons.
- Carbon-14 (or ^{14}C) has the atomic number 6 and mass number 14 (six protons and eight neutrons). It contains six protons, eight neutrons, and six electrons

When reading a specific isotope symbol, it is read as "element, mass number." For instance, in the case of magnesium, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." All magnesium atoms have the atomic number 12, which means they have 12 protons in their nucleus. These isotopes differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg atom has 14 neutrons.

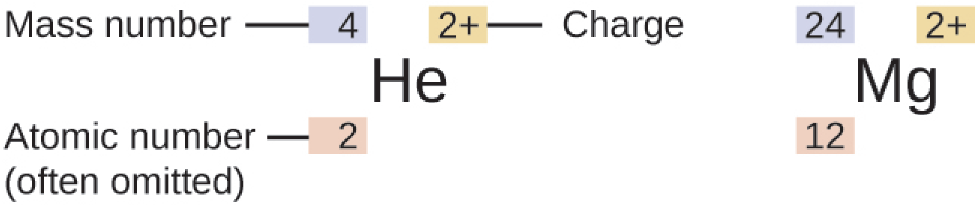

Figure 5.5b Atomic Symbols used to Represent Isotopes of Elements: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge of its ion as a right superscript. Isotopes for Helium-4 and Magnesium-24 are shown in this figure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 5.5a

Provide the isotope short form and isotope symbol (include the mass number only, omit atomic number) for the following isotopes: Arsenic-74, Calcium-44. Refer to the periodic table if needed.

Solution

Arsenic-74: Isotope short form = As-74; isotope symbol = ^{74}As

Calcium-44: Isotope short form = Ca-44; isotope symbol = ^{44}Ca

Example 5.5b

Provide the correct name for the isotope having the symbol ^{202}Hg; ^{56}Fe. Refer to the periodic table if needed.

Solution

^{202}Hg; Isotope name = Mercury-202

^{56}Fe; Isotope name = Iron – 56

Example 5.5c

Write the isotope name and symbol (mass number only) for the following two elements. Refer to the periodic table if needed.

- Element 1 has 12 protons and 13 neutrons
- Element 2 has 17 protons and 20 neutrons

Solution

Element 1 has 12 protons (therefore its atomic number is 12). Using a periodic table for reference, the element with atomic number 12 is Magnesium (Mg). The mass number will be 12 p^+ + 13 n^0 = 25.

Isotope Name = Magnesium-25 or Mg-25

Isotope Symbol = ^{25}Mg

Element 2 has 17 protons (therefore its atomic number is 17). Using a periodic table for reference, the element with atomic number 17 is chlorine (Cl). The mass number will be 17 p^+ + 20 n^0 = 37.

Isotope Name = Chlorine-37 or Cl-37

Isotope Symbol = ^{37}Cl

Exercise 5.5a

Check Your Learning Exercise (Text Version)
Choose the option that best answers the statements for each of the provided multiple choice questions.

1. Isotopes differ in the number of

    a. orbitals
    b. protons
    c. neutrons
    d. electrons
    e. charges

2. Hydrogen has three naturally occurring isotopes. Which of the following is not an isotope of hydrogen?

    a. Quatrium, ^{4}H, contains one electron, one proton, and three neutrons
    b. Tritium, ^{3}H, contains one electron, one proton, and two neutrons
    c. Deuterium, has symbol ^{2}H, contains one electron, one proton, and one neutron
    d. Protium, has symbol ^{1}H, contains one electron, one proton, and no neutrons

3. The isotope short form and isotope symbol (include the mass number only, omit atomic number) for Iodine-127 is

    a. I-127; ^{127}I
    b. I-127; $_{127}$I
    c. Io-127; ^{127}Io
    d. I-53; ^{53}I
    e. I-74; ^{74}I

4. Which of the following is the isotope symbol (include the mass number only, omit atomic number) for the atom that has 15 protons and 16 neutrons.

    a. ^{16}O
    b. ^{31}Ga
    c. ^{15}P
    d. ^{16}P
    e. ^{31}P

5. The isotope name and short form for a neutral atom that has with 7 electrons and 8 neutrons is

    a. nitrogen – 8; N-8
    b. nitrogen – 14; N-14
    c. nitrogen – 15; N-15
    d. oxygen – 14; O-14
    e. oxygen – 15; O-15

6. Tin is a silvery malleable metallic element belonging to group 14 of the periodic table. Tin has many stable naturally occurring isotopes, including tin–120, which has a natural abundance of 32.58%. Which of the following is true of the isotope tin-120?

   a. As a neutral isotope, it contains 50 protons, 50 electrons, and 70 neutrons
   b. Its mass number is 120
   c. Its atomic number is 50
   d. Its isotope symbol is 120Sn
   e. all of these options contain true information about tin-120

7. The element X in an atom with a mass number (A) of 33 and atomic number (Z) 16 is

   a. Arsenic
   b. Indium
   c. Sulfur
   d. Chlorine
   e. none of these elements represent this isotope

8. Which of the following is element X in an atom with a mass number of 58 and contains 30 neutrons?

   a. Cobalt
   b. Copper
   c. Cerium
   d. Nickel
   e. Zinc

Check Your Answer[1]

Source: "Exercise 5.5a" by Jackie MacDonald, licensed under CC BY-NC-SA 4.0.

While the atomic mass (mass number) of individual isotopes of a given element is different, their physical and chemical properties remain mostly the same. However, isotopes do differ in their stability. Carbon-12 (^{12}C) is the most abundant of the carbon isotopes, accounting for 98.93% of carbon on Earth. Carbon-13 (^{13}C) is stable but only accounts for about 1.07% abundance in nature. Carbon-14 (^{14}C) isotopes are found in trace amounts in nature and are unstable or radioactive. Radioactive isotopes may decay over time by emitting neutrons, protons, and/or electrons and energy to obtain a more stable form. Further information relating to radioactivity/radioactive decay would be covered in more detail in nuclear chemistry or nuclear physics.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 5.5a. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^3H, is also called tritium and sometimes symbolized T.

Table 5.5a Nuclear Compositions of Atoms of the Very Light Elements (modified by Jackie MacDonald to include "mass number" column)

Isotope Name	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass Number	Mass (amu)	% Natural Abundance
hydrogen-1 (protium)	${}^{1}_{1}\mathrm{H}$	1	1	0	1	1.0078	99.989
hydrogen-2 (deuterium)	${}^{2}_{1}\mathrm{H}$	1	1	1	2	2.0141	0.0115
hydrogen-3 (tritium)	${}^{3}_{1}\mathrm{H}$	1	1	2	3	3.01605	— (trace)
helium-3	${}^{3}_{2}\mathrm{He}$	2	2	1	3	3.01603	0.00013
helium-4	${}^{4}_{2}\mathrm{He}$	2	2	2	4	4.0026	100
lithium-6	${}^{6}_{3}\mathrm{Li}$	3	3	3	6	6.0151	7.59
lithium-7	${}^{7}_{3}\mathrm{Li}$	3	3	4	7	7.0160	92.41
beryllium-9	${}^{9}_{4}\mathrm{Be}$	4	4	5	9	9.0122	100
boron-10	${}^{10}_{5}\mathrm{B}$	5	5	5	10	10.0129	19.9
boron-11	${}^{11}_{5}\mathrm{B}$	5	5	6	11	11.0093	80.1
carbon-12	${}^{12}_{6}\mathrm{C}$	6	6	6	12	12.0000	98.89
carbon-13	${}^{13}_{6}\mathrm{C}$	6	6	7	13	13.0034	1.11
carbon-14	${}^{14}_{6}\mathrm{C}$	6	6	8	14	14.0032	— (trace)
nitrogen-14	${}^{14}_{7}\mathrm{N}$	7	7	7	14	14.0031	99.63
nitrogen-15	${}^{15}_{7}\mathrm{N}$	7	7	8	15	15.0001	0.37
oxygen-16	${}^{16}_{8}\mathrm{O}$	8	8	8	16	15.9949	99.757
oxygen-17	${}^{17}_{8}\mathrm{O}$	8	8	9	17	16.9991	0.038
oxygen-18	${}^{18}_{8}\mathrm{O}$	8	8	10	18	17.9992	0.205

Isotope Name	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass Number	Mass (amu)	% Natural Abundance
fluorine-19	$^{19}_{9}\text{F}$	9	9	10	19	18.9984	100
neon-20	$^{20}_{10}\text{Ne}$	10	10	10	20	19.9924	90.48
neon-21	$^{21}_{10}\text{Ne}$	10	10	11	21	20.9938	0.27
neon-22	$^{22}_{10}\text{Ne}$	10	10	12	22	21.9914	9.25

In Exercise 5.5b, choose the ISOTOPES simulator option to explore different isotopes of the first 10 elements. Be sure to expand and review the atomic symbol and abundance in nature data when comparing isotopes. To create isotopes of a given element, choose your element, for example carbon, then add or remove neutrons. Observe what happens to the element symbol, the abundance in nature (%), and its stability.

Exercise 5.5b

Practice using the following PhET simulation: Isotopes and Atomic Mass

Scientists in Action: Mildred Cohn, PhD.

As you will learn, isotopes are important in nature and especially in human understanding of science and medicine. Let's consider just one natural, stable isotope: Oxygen-18, which is noted in the Table 5.5a above and is referred to as one of the environmental isotopes. It is important in paleoclimatology, for example, because scientists can use the ratio between Oxygen-18 and Oxygen-16 in an ice core to determine the temperature of precipitation over time. Oxygen-18 (Figure 5.5c) was also critical to the discovery of metabolic pathways and the mechanisms of enzymes.

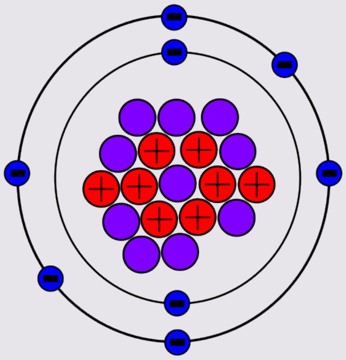

Figure 5.5c Oxygen-18 Atom: The isotope, oxygen-18, includes 8 protons and 10 neutrons in the core nucleus, and 8 electrons around the nucleus. (credit: work by SM358, PD).

Mildred Cohn pioneered the usage of these isotopes to act as tracers, so that researchers could follow their path through reactions and gain a better understanding of what is happening. One of her first discoveries provided insight into the phosphorylation of glucose that takes place in mitochondria. And the methods of using isotopes for this research contributed to entire fields of study.

Learn more about Mildred Cohn's work and her motivating story of overcoming gender and religious biases in the article Mildren Cohn (1913-2009) [New Tab].

WATCH Women in Chemistry: Mildred Cohn (18min 42sec).

Attribution & References

Except where otherwise noted, this page is adapted by Jackie MacDonald from "2.3 – Atomic Structure and Symbolism " In *Chemistry 2e (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson is licensed under CC BY 4.0. Access for free at *Chemistry 2e (Open Stax)* / Reused section on isotopes, rewrote learning objectives.

Notes

1. (1) c; (2) a; (3) a; (4) e; (5) c; (6) e; (7) c; (8)d

5.6 ATOMIC MASS

Learning Objectives

By the end of this section, you will be able to:

- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 5.6a).

Figure 5.6a Perspective about an Atoms Relative Size: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by babyknight, CC BY 2.0; credit right: modification of work by Paxson Woelber, CC BY 2.0)

Watch Just How Small is an Atom? (5:27 min)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the **atomic mass unit (amu)** and the **fundamental unit of charge (e)**. The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12"). Thus, one amu is exactly $\frac{1}{12}$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The **Dalton (Da)** and the **unified atomic mass unit (u)** are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton). The properties of these fundamental particles are summarized in Table 5.6a. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass. The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00 amu. This "missing" mass is known as the mass defect, which you can learn about it if you study nuclear chemistry.)

Table 5.6a Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the **atomic mass** of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes, each with their own slightly different masses due to the different number of neutrons they contain.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129\text{ amu}) + (0.801 \times 11.0093\text{ amu})\\ &= 1.99\text{ amu} + 8.82\text{ amu}\\ &= 10.81\text{ amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Exercise 5.6a

Calculating Average Atomic Mass

5.6a – Calculating Average Atomic Mass (Text version)
A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution
STEP 1 – List known quantities and identify what you are asked to find

Known information: Isotopes of neon – 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu).

What am I asked to Find: average mass of the neon in the solar wind

Step 2 – Determine how you will solve the problem

Use the following formula to solve problem:

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

Step 3 – Solve the Problem

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924 \text{ amu}) + (0.0047 \times 20.9940 \text{ amu}) + (0.0769 \times 21.9914 \text{ amu}) \\ &= (18.36 + 0.099 + 1.69) \text{ amu} \\ &= 20.15 \text{ amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Step 4 – Does the answer make sense?

- Yes it does. It is similar to the average atomic mass of Ne on the periodic table. The average atomic mass is in between the given amu values for Ne-20, Ne-21 and Ne-22, and the average amu value calculated is closest to the most abundant isotope, Ne-20.

Source: "Exercise 5.6a" by Jackie MacDonald, licensed under CC BY-SA 4.0.

If you want to review additional examples of how to calculate average atomic mass, **Watch How to Calculate Atomic Mass Practice Problems (6 mins 10s)**

Exercise 5.6b

Calculating Average Atomic Mass

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Check Your Answer[1]

We can also do variations of this type of calculation where you calculate the percent abundance of each isotope, as shown in the next example:

Example 5.6b

Calculating Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

Step 1 – List known quantities and identify what you are asked to find

Known information: ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with copper having an average atomic mass of 35.453 amu

What am I asked to Find: What is the percent composition of Cl in terms of these two isotopes

Step 2 – Determine how you will solve the problem

Use the following formula to solve problem:

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \ \times \ \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \ \times \ \text{mass of } ^{37}\text{Cl})$$

If we let *x* represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by 1.00 − *x*.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 – the fraction of ^{35}Cl.)

Step 3 – Solve the Problem

Substituting this into the average mass equation, we have:

$$\begin{aligned} 35.453\text{ amu} &= (x \times 34.96885\text{ amu}) + [(1.00 - x) \times 36.96590\text{ amu}] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576 \end{aligned}$$

So solving yields: x = 0.7576, which means that 1.00 – 0.7576 = 0.2424. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl.

Step 4 – Does the answer make sense?

Yes it does. The highest % abundance found is ^{35}Cl ; which has a mass of 34.96885 amu is closest to the average mass of Cu, which is 35.453 amu.

If you want to watch the full work through of Example 5.6b – Calculation of Percent Abundance, **Watch How to Calculate Isotope Abundance (11 mins 48s)**

Exercise 5.6c

Calculation of Percent Abundance

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Check Your Answer[2]

Try the interactive learning activity suggested below to reinforce your learning about isotope ratios and atomic mass. Try make mixtures of the main isotopes of the first 18 elements, gain experience with average atomic mass, and check naturally occurring isotope ratios using the Isotopes and Atomic Mass simulation.

Exercise 5.6d

Practice using the following PhET simulation: Isotopes and Atomic Mass

Determining Natural Abundances of Isotopes using Mass Spectrometry.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 5.6b), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.

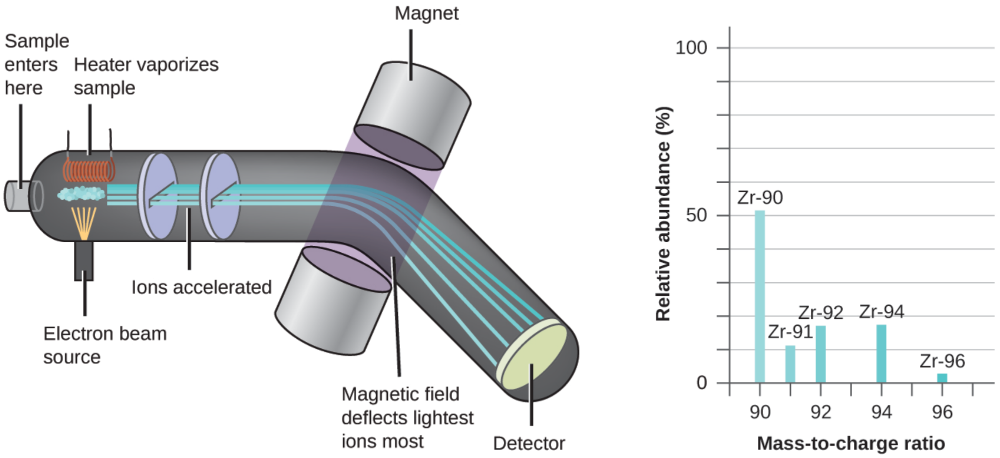

Figure 5.6b A Typical Mass Spectrometer: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch Mass Spectometry (8:19 min)

Watch Mass Spectrometry MS (7:58 min)

Key Equations

- $\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$

Attribution & References

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Notes

1. Step 1 - List known quantities and identify what you are asked to find
   Known information: 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu)
   What am I asked to Find: average mass of a Mg atom
   Step 2 - Determine how you will solve the problem
   Use the following formula to solve problem:
   $$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$
   Step 3 - Solve the Problem
   $$\begin{aligned}\text{average mass} &= (0.7870 \times 23.98\text{ amu}) + (0.1013 \times 24.99\text{ amu}) + (0.1117 \times 25.98\text{ amu}) \\ &= (18.872 + 2.531 + 2.902)\text{ amu} \\ &= 24.305\text{ amu}\end{aligned}$$
   Step 4 - Does the answer make sense?
   - Yes it does. It is similar to the average atomic mass of Mg on the periodic table. The average atomic mass is in between the given amu values for Ne-20, Ne-21 and Ne-22, and the average amu value calculated is a bit more than the most abundant isotope, Mg-24.
2. Step 1 - List known quantities and identify what you are asked to find
   Known information: ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu.
   What am I asked to Find:What is the percent composition of Cu in terms of these two isotopes?
   Step 2 - Determine how you will solve the problem
   Use the following formula to solve problem:

The average mass of Copper is the fraction that is ^{63}Cu times the mass of ^{63}Cu plus the fraction that is ^{65}Cu times the mass of ^{65}Cu

$$\text{average mass} = (\text{fraction of } ^{63}\text{Cu } \times \text{ mass of } ^{63}\text{Cu}) + (\text{fraction of } ^{65}\text{Cu } \times \text{ mass of } ^{65}\text{Cu})$$

If we let *x* represent the fraction that is ^{63}Cu, then the fraction that is ^{65}Cu is represented by 1.00 – *x*.
(The fraction that is ^{63}Cu + the fraction that is ^{65}Cu must add up to 1, so the fraction of ^{63}Cu must equal 1.00 – the fraction of ^{65}Cu.) Step 3 - Solve the Problem

$$\begin{aligned} 63.546 \text{ amu} &= (x \times 62.9296 \text{ amu}) + [(1.00 - x) \times 64.9278 \text{ amu}] \\ 63.546 &= 62.9296x + 64.9278 - 64.9278x \\ 1.9982x &= 1.3818 \\ x &= \frac{1.3818}{1.9982} = 0.6915 \end{aligned}$$

So solving yields: *x* = 0.6915, which means that 1.00 – 0.6915= 0.3085. Therefore, chlorine consists of 69.15% of Cu-63 and and 30.85% Cu-65

Step 4 - Does the answer make sense?

Yes it does. The highest % abundance found is Cu-63, which has a mass of 62.9296 amu is closest to the average mass of Cu, which is 63.546 amu.

CHAPTER 5 - SUMMARY

5.1 Early Atomic Theory: Dalton's Model of the Atom

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that matter is composed of exceedingly small, indivisible particles called atoms. He also stated an atom is the smallest unit of an element that can participate in a chemical change and that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

5.2 Electric Charge

Ancient Greek philosopher, Thales of Miletus (624–546 BCE), recorded that when amber (a hard, translucent, fossilized resin from extinct trees) was vigorously rubbed with a piece of fur, a force was created that caused the fur and the amber to be attracted to each other. The rubbed amber would not only attract the fur, and the fur attract the amber, but they both could affect other (nonmetallic) objects, even if not in contact with those objects.

The English physicist William Gilbert (1544–1603) completed similar experiments with similar findings. It was concluded there were two types of electric charge – positive and negative. These forces are repulsive when the same type of charge exists on two interacting objects. These forces are attractive when the charges are of opposite types. The force acts by contact or induction. The magnitude of the force decreases (rapidly) as the objects move further away from each other. Whereas, the magnitude of the force increases (rapidly) as the objects move closer to each other. Finally, not all matter is affected by this electric force.

5.3 Subatomic Particles of the Atom

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called electrons embedded in a positive atomic space. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford's gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons.

5.4 Defining the Nuclear Atom

Experimental observations provided insight into the structure of the nuclear atom. The majority of the atom's structure is made up of empty space, with a centrally located, very concentrated nucleus. The nucleus contains positively charged protons and neutrally charged neutrons. Combined, these two subatomic particles account for the majority of the mass in a given atom. The negative electrons, which contribute very little to the overall mass of the atom, are in orbit around the nucleus within the empty space. The type of element is determined by the number of protons in the nucleus of the atom. Every element has a specific atomic number that equals the number of protons it contains; an element's atomic number can sourced from the periodic table.

The number of protons, neutrons, and electrons an atom contains differentiates one type of atom from the next. In any given atom of an element when the number of positively charged protons and the number of negatively charged electrons are the same, the atom is neutral. An atom that loses or gains electrons is called an ion. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms called cations are formed when an atom loses one or more electrons.

5.5 Isotopes of the Elements

Isotopes are various forms of the same element that have the same number of protons but a different number of neutrons. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number not only indicates the number of protons but also the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A). Atomic symbols for elements are used to represent specific isotopes of atoms and include their mass number (A) in superscript, atomic number (Z) in subscript, followed by the element symbol.

In summary:

$$\begin{aligned}\text{atomic number (Z)} &\quad \text{number of protons}\\ \text{mass number (A)} &\quad \text{number of protons} + \text{number of neutrons}\\ \text{A - Z} &\quad \text{number of neutrons}\end{aligned}$$

When reading a specific isotope symbol, it is read as "element, mass number." For instance, in the case of magnesium, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24."

5.6 Atomic Mass

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $\frac{1}{12}$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus, so each isotope will have a slightly different atomic mass. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved, and this number is represented on a periodic table for each element. Average atomic masses and percent abundance for each element's isotopes can be calculated using formulas.

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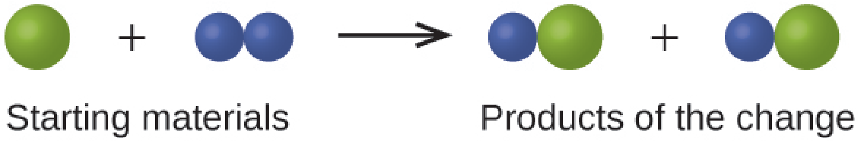
CHAPTER 5 - REVIEW

5.1 Early Atomic Theory: Dalton's Model of the Atom

1. In the following drawing, the green, larger spheres represent atoms of a certain element. The blue, smaller spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?


Check Answer: [1]
2. Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.
Check Answer: [2]
3. Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.
Check Answer: [3]
4. Samples of compound X, Y, and Z are analyzed, with results shown in the data table below.

Qualitative and Quantitative Analysis of Compounds X, Y, Z

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colourless, liquid with strong odour	1.776 g	0.148 g
Y	clear, colourless, liquid with strong odour	1.974 g	0.329 g
Z	clear, colourless, liquid with strong odour	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z? **Check Answer:** [4]

5. For the following questions, state whether the statement regarding Dalton's Atomic Theory is True or False. If it is false, provide the correct word or phrase for the **bolded** term to make that statement true.
   a. According to Dalton's Atomic Theory, matter consists of indivisible particles called **atoms**.
   b. Dalton's Atomic Theory postulates mass is neither created nor destroyed in a chemical reaction. This supports the **law of constant proportions**.

   c. According to Dalton's atomic theory, all atoms of a given element have identical **properties** including identical **mass**.
   d. Two of Dalton's postulates include (1) matter is composed of exceedingly small, indivisible particles and (2) elements consist of only one type of identical atom, which has the same mass for all atoms. These two theories have been proven to be **valid** theories by later scientists.
      Check Answer: [5]

5.2 Electric Charge

1. For the following questions, state whether the statement regarding electric charge is True or False. If it is false, provide the correct word or phrase for the **bolded** term to make that statement true.
   a. Electric charges can be **positive** and negative.
   b. Electric force can be either be **equal** or repulsive.
   c. If two interacting objects carry opposite charges, it results in electrostatic **repulsion**.
   d. A balloon is rubbed on hair to gain charge. Then the comb is placed near running water from a tap. You observe that the stream of water is bending towards the comb. You conclude that the comb and water must have **similar** charges.
      Check Answer: [6]
2. Does the force of attraction increase, decrease, or stay the same as the distance decreases between two oppositely charged objects (as the objects near one another)?
   Check Answer: [7]
3. Does the force of attraction increase, decrease, or stay the same as the distance increases between two oppositely charged objects (as the objects get further from one another)?
   Check Answer: [8]
4. Explain what is meant by induction in reference to electric forces.
   Check Answer: [9]

5.3 Subatomic Particles of the Atom

1. How are electrons and protons similar? How are they different?
   Check Answer: [10]
2. How are protons and neutrons similar? How are they different?
3. **Check Answer:** [11]
4. Predict and test the behaviour of α particles fired at a "plum pudding" model atom.
   a. Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.

   b. If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
   c. Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.
   Check Answer: [12]
5. Predict and test the behaviour of α particles fired at a Rutherford atom model.
   a. Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.
   b. If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
   c. Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?
   d. Now test your predictions from (a), (b), and (c). Open the Rutherford Scattering simulation and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.
   Check Answer: [13]

5.4 Defining the Nuclear Atom

1. Describe the structure of the nuclear atom as proposed by Rutherford.
   Check Answer: [14]
2. Write the ion symbol for each of the following ions and state whether it is an anion or a cation.
   a. the ion with atomic number 55, 54 electrons, and mass number 133
   b. the ion with 54 electrons, 53 protons

    c. the ion with atomic number 15 and a 3– charge
    d. the ion with 24 electrons, and a 3+ charge (Hint – the neutral atom would have lost electrons to form this positive ion).
    Check Answer: [15]
3. Write the ion symbol for each of the following ions:
    a. the ion with a 3+ charge, 31 protons
    b. the ion with 36 electrons, 35 protons
    c. the ion with 86 electrons, and a 4+ charge
    d. the ion with a 2+ charge, atomic number 38
    Check Answer: [16]
4. Open the Build an Atom simulation – Choose the ATOM simulation. Expand the net charge and mass number options by clicking on the + icon.
    a. Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium that gives a mass number of 6. Write the element symbol for a neutral lithium atom.
    b. Now remove one electron to make an ion. What is the ion's net charge? Give the symbol for the ion you have created.
    Check Answer: [17]
5. Open the Build an Atom simulation – Choose the ATOM simulation. Expand the net charge and mass number options by clicking on the + icon.
    a. Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Nitrogen that gives a mass number of 14. How many protons, neutrons, and electrons are there in this nitrogen atom?
    b. Write the element symbol for a neutral Nitrogen atom.
    c. Now add three electrons to make an ion. How many TOTAL electrons are now in this nitrogen atom? What is the ion's net charge? Give the symbol for the ion you have created.
    Check Answer: [18]

5.5 Isotopes of Elements

1. In what way are isotopes of a given element always different? In what way(s) are they always the same?
    Check Answer: [19]
2. Write the isotope symbol for each of the following neutral elements:
    a. atomic number 55, mass number 133
    b. 53 protons, 74 neutrons
    c. 15 electrons, mass number 31
    d. atomic number 27, 30 neutrons
    Check Answer: [20]

3. Write the isotope symbol for each of the following neutral elements:
    a. 31 electrons, and a mass number of 71
    b. 35 protons, and 45 neutrons
    c. atomic number 90, 142 neutrons
    d. 38 protons, and mass number 87
    Check Answer: [21]
4. Open the Build an Atom simulation and click on the Atom icon.
    a. Pick any one of the first 10 elements that you would like to build and state its symbol.
    b. Drag protons, neutrons, and electrons onto the atom template to make an atom of your element. State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.
    c. Click on "Net Charge" and "Mass Number," check your answers to (b), and correct, if needed.
    d. Predict whether your atom will be stable or unstable. State your reasoning.
    e. Check the "Stable/Unstable" box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.
    Check Answer: [22]
5. Open the Build an Atom simulation
    a. Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.
    b. Now add two more electrons to make an ion and give the symbol for the ion you have created.
    Check Answer: [23]
6. Open the Build an Atom simulation
    a. Drag protons, neutrons, and electrons onto the atom template to make a neutral atom, stable atom of Fluorine. How many protons, neutrons, and electrons does this stable isotope have? What is the mass number of this stable isotope? Give the isotope symbol for this atom.
    Check Answer: [24]
7. Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses and name each element. Then, give the isotope symbol including atomic number, mass number and ion charge:
    a. atomic number 9, mass number 18, charge of 1−
    b. atomic number 43, mass number 99, charge of 7+
    c. atomic number 53, atomic mass number 131, charge of 1−
    d. atomic number 81, atomic mass number 201, charge of 1+
    e. Name the elements in parts (a), (b), (c), and (d).
    Check Answer: [25]
8. The following are properties of isotopes of two elements that are essential in our diet. Determine the

number of protons, neutrons and electrons in each and name the isotope.

   a. atomic number 26, mass number 58, charge of 2+
   b. atomic number 53, mass number 127, charge of 1–

   Check Answer: [26]

9. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes. Name the element:
   a. ${}^{10}_{5}\mathrm{B}$
   b. ${}^{199}_{80}\mathrm{Hg}$
   c. ${}^{63}_{29}\mathrm{Cu}$
   d. ${}^{13}_{6}\mathrm{C}$
   e. ${}^{77}_{34}\mathrm{Se}$

   Check Answer: [27]

10. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:
    a. ${}^{7}_{3}\mathrm{Li}$
    b. ${}^{125}_{52}\mathrm{Te}$
    c. ${}^{109}_{47}\mathrm{Ag}$
    d. ${}^{15}_{7}\mathrm{N}$
    e. ${}^{31}_{15}\mathrm{P}$

    Check Answer: [28]

11. Click on the Isotopes and Atomic Mass Simulation and select the "Mixtures" simulation option. Then under the isotope mixture option choose "My Mix". Hide the "Percent Composition" and "Average Atomic Mass" boxes, and then select the element boron (B).
    a. Write the symbols of the isotopes of boron that are provided (naturally occurring) in significant amounts.
    b. Predict the relative amounts (percentages) of these boron isotopes found in nature. % of isotope 1 vs % of isotope 2 of boron. Explain the reasoning behind your choice. (hint – reference your periodic table for an elements atomic mass).
    c. Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on "More" and then move the sliders to the appropriate amounts.
    d. Reveal the "Percent Composition" and "Average Atomic Mass" boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.
    e. Select "Nature's" mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match "Nature's" amounts as closely as possible.

    Check Answer: [29]

12. Repeat Chemistry End of Chapter Exercise 11 (a-e) using the PhET isotopes and atomic mass

simulation and choose the element Silicon, which has three naturally occurring isotopes. **Check Answer:** [30]

5.6 Atomic Mass

1. An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element. Write the name and element symbol for this element.
   Check Answer: [31]
2. Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu) and abundances (50.69% and 49.31%) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.
   Check Answer: [32]
3. Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.
   Check Answer: [33]
4. The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.0931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.
   Check Answer: [34]
5. The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?
   Check Answer: [35]

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BY 4.0. Access for free at *Chemistry 2e (Open Stax)*. / Additional questions created and added by Jackie MacDonald.

Notes

1. The starting materials consist of one green, larger sphere and two blue, smaller spheres. The products consist of two green spheres and two blue spheres. This violates Dalton's theory that that atoms are not created during a chemical change, but are merely redistributed.
2. Atoms are neither created nor destroyed during a chemical change
3. This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.
4. X+Z have the same ratios of C and H and are therefore similar compounds, and is an example of the Law of Definite Proportions; however, they may or may not be the same compound. Samples from two unknown compounds that have the same mass ratio are not necessarily the same substance. Example: formaldehyde (CH_2O) and glyceraldehyde ($C_3H_6O_3$) have the same mass ratios but are not the same compound. X+Y and Y+Z have differing ratios of C and H and are therefore different compounds, aligning with the Law of Multiple Proportions. View an explanation of the solution in the video "Problem 2.1.3"
5. (a) TRUE; (b) FALSE - Law of conservation of mass; (c) TRUE (d) FALSE - Invalid
6. (a) TRUE; (b) FALSE – attractive; (c)FALSE – attraction; (d) FALSE - opposite
7. The force of attraction **increases** as the distance decreases between two oppositely charged objects (as the objects near one another the force of attraction is greater / gets stronger).
8. The force of attraction **decreases** as the distance increases between two oppositely charged objects (as the objects get further from one another the attractive force between the two objects lessens / gets weaker)
9. Induction is a method used to charge an object without actually touching the object to any other charged object.
10. Protons reside in an atom's nucleus; whereas electrons reside outside the nucleus in the space around the nucleus. Electrons can freely move around nucleus of the atom. Electrons are a type of subatomic particle with a negative charge; whereas protons are a type of subatomic particle with a positive charge. Mass of the proton is found to be 1.673 x 10^{-24} g, which is 1,836 times the mass of an electron.
11. Both protons and neutrons are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.
12. See written answers below. For a video demonstration of this answer view "2.8 | Predict and test the behaviour of α particles fired at a "plum pudding" model atom. (a) Predict" 3(a) This is a prediction; your prediction may be different than shown here. Most of the α alpha particles should repel the atoms in the structure and would not directly go through since the positive charge in the plum pudding model was assumed to be spread out throughout the entire volume of the atom. They would be redirected and deflected in many areas.3(b) This is a prediction; your prediction may be different than shown here. α alpha particles of higher energy would be moving faster and reacting faster. They would still come in contact with the positive charges scattered throughout the atom and will be deflected faster in many directions due to higher energy state.3(c) Your answer may be YES or NO depending on the predictions you made. The predictions listed above did not match what happened in the simulation for question (a) and (b). In the simulation, the majority of the α alpha particles passed straight through the plum pudding model. This is because the positive charge in the plum pudding model was assumed to be spread out throughout the entire volume of the atom and so were the oppositely charged electrons. Therefore, the electric field from the positively charged "pudding" would be too weak to significantly affect the path of the relatively massive particles moving at slower (lower energy) or faster speeds (higher energy).

13. See written answers below. For a video demonstration of this answer view the video "2.9 | Predict and test the behaviour of α particles fired at a Rutherford atom model." (a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be.4(b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection.4(c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger.4(d) The paths followed by the α particles match the predictions from (a), (b), and (c).
14. The majority of the atom's structure is made up of empty space, with a centrally located, very concentrated nucleus. The three major subatomic particles are protons, neutrons, and electrons. The nucleus contains positively charged protons and neutrally charged neutrons. Combined, these account for most of the mass in a given atom. The negative electrons, which contribute very little to the overall mass of the atom, are in orbit around the nucleus within the empty space.
15. (a) Cs^{+} - cation; (b) I^{-} - anion; (c) P^{3-} - anion; (d) Co^{3+} - cation
16. (a) Ga^{3+} (b) Br^{-} (c) Th^{4+} (d) Sr^{2+}
17. (a) Symbol for neutral lithium atom (3 protons, 3 neutrons and 3 electrons) is Li; (b) By removing one electron lithium atom now has only 2 electrons but still 3 protons. The ion's net charge is +1. The symbol for the lithium ion is Li^{+}.
18. (a) There are 7 protons, 7 neutrons, and 7 electrons in the nitrogen atom; (b) N symbol for neutral atom is N; (c) TOTAL electrons = 7+3 = 10 electrons in nitrogen ion. Its net ionic charge is 3- or -3. Ion symbol is N^{3-}.
19. Isotopes of a given element always have different masses due to different numbers of neutrons. They always have the same number of protons, which determines the identity of the element.
20. (a) $^{133}_{55}\text{Cs}$ (b) $^{127}_{53}\text{I}$ (c) $^{31}_{15}\text{P}$ (d) $^{57}_{27}\text{Co}$
21. (a) $^{71}_{31}\text{Ga}$ (b) $^{80}_{35}\text{Br}$ (c) $^{232}_{90}\text{Th}$ (d) $^{87}_{38}\text{Sr}$
22. This is just one example of an answer the first ten elements - the element Nitrogen was chosen. You may have chosen a different atom and therefore would have different answers. (a) Nitrogen symbol is N; (b) We built an atom with 7 protons, 7 electrons and 7 neutrons; the net charge is 0; mass number is 14 (number of protons + number of neutrons); (c) our answers check correctly with the simulation. (c) We predict the nitrogen atom we build with be stable. The number of protons and neutrons are a similar number and are likely to be a stable isotope that occurs naturally. (d) when stable/stable is checked off, our element is STABLE; if it was unstable, you would add or take away neutrons until the simulation shows a stable isotope. Nitrogen-15 (has 8 neutrons) is also a stable isotope of nitrogen. However nitrogen atoms with 6 or less or 9 or more neutrons are unstable. As a result, they are not abundant in nature.
23. (a) Oxygen-16 isotope symbol is $^{16}_{8}\text{O}$ (b) O^{2-}
24. A neutral, stable atom of fluorine will have 9 protons, 9 electrons, and 10 neutrons. Mass number is 19 (number of protons + number of neutrons); Isotope symbol for Fluorine-19 is $^{19}_{9}\text{F}$
25. (a) 9 protons, 9 neutrons, 10 electrons in fluorine; $^{18}_{9}\text{F}^{-}$ (b) 43 protons, 56 neutrons, 36 electrons in Technetium; $^{99}_{43}\text{Tc}^{7+}$ (c) 53 protons, 78 neutrons, 54 electrons in Iodine $^{131}_{53}\text{I}^{-}$ (d) 81 protons, 120 neutrons, 80 electrons in Thallium; $^{201}_{81}\text{Tl}^{+}$
26. (a) 26 protons, 32 neutrons, 24 electrons; Iron-58 (b) 53 protons, 74 neutrons, 54 electrons; Iodine-127
27. (a) 5 protons, 5 electrons, 5 neutrons; Boron (b) 80 protons, 80 electrons, 119 neutrons; Mercury (c) 29 protons, 29 electrons, 34 neutrons; Copper (d) 6 protons, 6 electrons, 7 neutrons; Carbon (e) 34 protons, 34 electrons, 43 neutrons; Selenium

28. (a) 3 protons, 3 electrons, 4 neutrons; Lithium (b) 52 protons, 52 electrons, 73 neutrons; Tellurium (c) 47 protons, 47 electrons, 62 neutrons; Silver (d) 7 protons, 7 electrons, 8 neutrons; Nitrogen (e) 15 protons, 15 electrons, 16 neutrons; Phosphorus
29. (a) There are two isotopes, boron-10 and boron-11. (b) There is no way to be sure to accurately predict the abundances to give you an answer of 10.81 amu average atomic mass for boron, as shown on periodic table. However, we can see that the average of 10.81 amu is closest to 11 amu, so the natural abundances will contain more boron-11 isotopes than boron-10 isotopes. Let us guess that the abundances are 15% B-10, 85% B-11. The average mass would be (.15x10 + .85x11) 10.85 amu (you may have predicted different percentages - it is just a prediction). (e) Checking the nature's mix of isotopes for boron shows that the abundances are 19.9% B-10 and 80.1% for B-11, so our guessed amounts only had to be slightly adjusted.
30. Let us use neon as an example. Since there are three isotopes (Ne-20, Ne21, Ne-23), there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature's mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.
31. Average atomic mass of element = (0.9092 x 19.99) + (0.0026x20.99) + (0.0882 x 21.99) = 20.169 amu. This average atomic mass is similar to Neon (Ne).
32. Average atomic mass of Bromine = (0.5069 x 78.9183) + (0.4931 x 80.9163) = 79.904 amu
33.
34. Average atomic mass of naturally occurring lithium = (0.075x 6.01512) + (0.925 x 7.01600) = 6.941 amu; Average atomic mass of commercial sourced lithium = (0.0375x 6.01512) + (0.9625 x 7.01600) = 6.978 amu
35. Turkey source: Equation used to solve is 10.807 = (x)10.0129x + (1-x)(11.0931) ANSWER: 26.49% of B-10 and 73.51% of B-11. US Source: 10.819 = (x)10.0129x + (1-x)(11.0931) ANSWER: 25.37 of B-10 and 74.63% of B-11.
36. The average mass of an oxygen atom in these meteorites will be great than an oxygen atom from earth since the meteorites contain more O-18 and less O-16 isotopes. Whereas on earth, the majority of the oxygen isotopes on earth are O-16. For a video demonstration of this answer view the video "2.26 | The O-18:O-16 abundance ratio"

CHAPTER 6. INORGANIC COMPOUND NOMENCLATURE

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

In this chapter, you will learn about

- Elements and their associated ions (cations and anions)
- Nomenclature
- Writing chemical formulas

- Naming binary ionic compounds
- Naming molecular compounds
- Naming acids

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Elements and ions
- Groups in the periodic table (metals and nonmetals)
- Formation of compounds

In this chapter, we will be learning about chemical nomenclature.

Chemical nomenclature is far too big a topic to treat comprehensively, and it would be a useless diversion to attempt to do so in a beginning course; most chemistry students pick up chemical names and the rules governing them as they go along. But we can hardly talk about chemistry without mentioning *some* chemical substances, all of which do have names— and often, more than one!

There are more than 100 million named chemical substances. Who thinks up the names for all these chemicals? Are we in danger of running out of new names? The answer to the last question is "no", for the simple reason that the vast majority of the names are not "thought up"; there are elaborate rules for assigning names to chemical substances on the basis of their structures. These are called *systematic names*; they may be a bit ponderous, but they uniquely identify a given substance. The rules for these names are defined by an international body. But in order to make indexing and identification easier, every known chemical substance has its own numeric "personal ID", known as a CAS registry number. For example, caffeine is uniquely identified by the registry number 58-08-2. About 15,000 new numbers are issued every day.

Common and Systematic Names

Many chemicals are so much a part of our life that we know them by their familiar names, just like our other friends. A given substance may have several common or *trivial names*; ordinary cane sugar, for example, is more formally known as "sucrose", but asking for it at the dinner table by that name will likely be a conversation-stopper, and I won't even venture to predict the outcome if you try using its systematic name in the same context:

"please pass the α-D-glucopyranosyl-(1,2)- β-D-fructofuranoside!"

But "sucrose" would be quite appropriate if you need to distinguish this particular sugar from the hundreds of other named sugars. The only place you would come across a systematic name like the rather unwieldy one mentioned here is when referring (in print or in a computer data base) to a sugar that has no common name.

Chemical substances have been a part the fabric of civilization and culture for thousands of years, and present-day chemistry retains a lot of this ancient baggage in the form of terms whose hidden cultural and historic connections add colour and interest to the subject. Many common chemical names have reached us only after remarkably long journeys through time and place, as the following two examples illustrate.

Ammonia

Most people can associate the name ammonia (NH_3) with a gas having a pungent odour; the systematic name "nitrogen trihydride" (which is rarely used) will tell you its formula. What it will not tell you is that smoke from burning camel dung (the staple fuel of North Africa) condenses on cool surfaces to form a crystalline deposit. The ancient Romans first noticed this on the walls and ceiling of the temple that the Egyptians had built to the Sun-god Amun in Thebes, and they named the material sal ammoniac, meaning "salt of Amun". In 1774, Joseph Priestly (the discoverer of oxygen) found that heating sal ammoniac produced a gas with a pungent odour, which a T. Bergman named "ammonia" eight years later.

Alcohol

Alcohol entered the English language in the 17th Century with the meaning of a "sublimated" substance, then became the "pure spirit" of anything, and only became associated with "spirit of wine" in 1753. Finally, in 1852, it become a part of chemical nomenclature that denoted a common class of organic compound. But it's still common practice to refer to the specific substance CH_3CH_2OH as "alcohol" rather then its systematic name *ethanol*.

Arabic alchemy has given us a number of chemical terms; for example, alcohol is believed to derive from Arabic or al-ghawl whose original meaning was a metallic powder used to darken women's eyelids (kohl).

Popular Names

The general practice among chemists is to use the more common chemical names whenever it is practical to do so, especially in spoken or informal written communication. For many of the very simplest compounds (including most of those you will encounter in a first-year course), the systematic and common names are the same, but where there is a difference and if the context permits it, the common name is usually preferred.

Many of the "common" names we refer to are known and used mainly by the scientific community. Chemical substances that are employed in the home, the arts, or in industry have acquired traditional or "popular" names that are still in wide use. Many, like sal ammoniac mentioned above, have fascinating stories to tell. Table 6a provides a list of popular names, their associated chemical names and their chemical formula.

Table 6a A list of popular names, their associated chemical name and formula.

popular name	chemical name	Formula
borax	sodium tetraborate decahydrate	$B_4O_7 \cdot 10H_2O$
calomel	mercury(I) chloride	Hg_2Cl_2
milk of magnesia	magnesium hydroxide	$Mg(OH)_2$
muriatic acid	hydrochloric acid	$HCl(aq)$
oil of vitriol	sulfuric acid	H_2SO_4
saltpeter	sodium nitrate	$NaNO_3$
slaked lime	calcium hydroxide	$Ca(OH)_2$

Minerals are solid materials that occur in the earth which are classified and named according to their compositions (which often vary over a continuous range) and the arrangement of the atoms in their crystal lattices. There are about 4000 named minerals. Many are named after places, people, or properties, and most frequently end with -ite.

Proprietary Names

Chemistry is a major industry, so it is not surprising that many substances are sold under trademarked names. This is especially common in the pharmaceutical industry, which uses computers to churn out names that they hope will distinguish a new product from those of its competitors. Perhaps the most famous of these is Aspirin, whose name was coined by the German company Bayer in 1899. This trade name was seized by the U.S. government following World War I, and is no longer a protected trademark in that country.

Attribution & References

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6.1 ELEMENTS AND THEIR IONS

Learning Objectives

By the end of this section, you will be able to:

- Define ions
- Identify ions on the periodic table

Ions

As a recap from Chapter 3, during the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 6.1a).

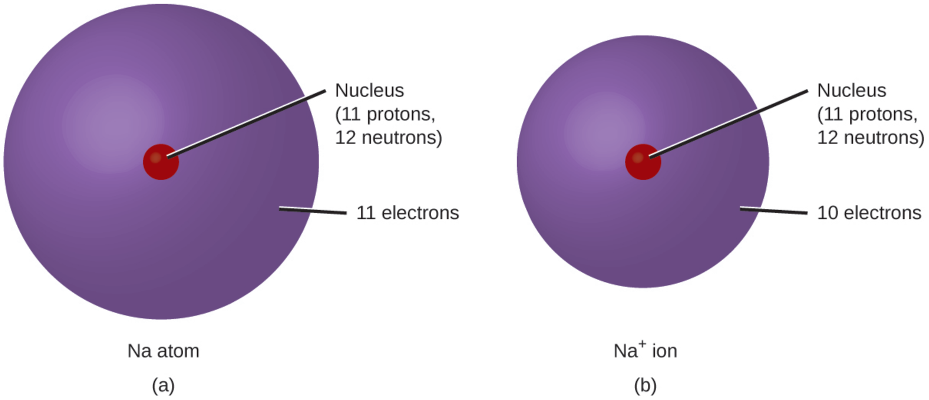

Figure 6.1a (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign (credit: *Chemistry (OpenStax)*, CC BY 4.0).

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^{-}. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 6.1b). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

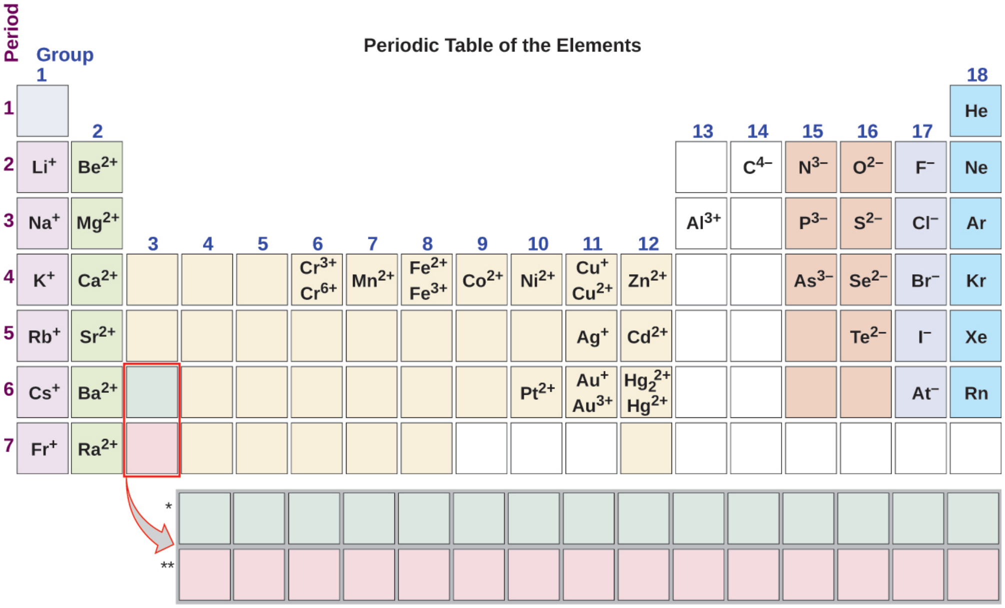

Figure 6.1b Some elements exhibit a regular pattern of ionic charge when they form ions. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 6.1a

Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

Exercise 6.1a

Give the symbol and name for the ion with 34 protons and 36 electrons.

Check Your Answer[1]

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom.

Links to Interactive Learning Tools

Explore Ion and Formula Writing from eCampusOntario H5P Studio.

Attribution & References

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Notes

1. Se^{2-}, the selenide ion

6.2 WRITING FORMULAS OF IONIC COMPOUNDS

Learning Objectives

By the end of this section, you will be able to:

- Define ionic compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure 6.2a).

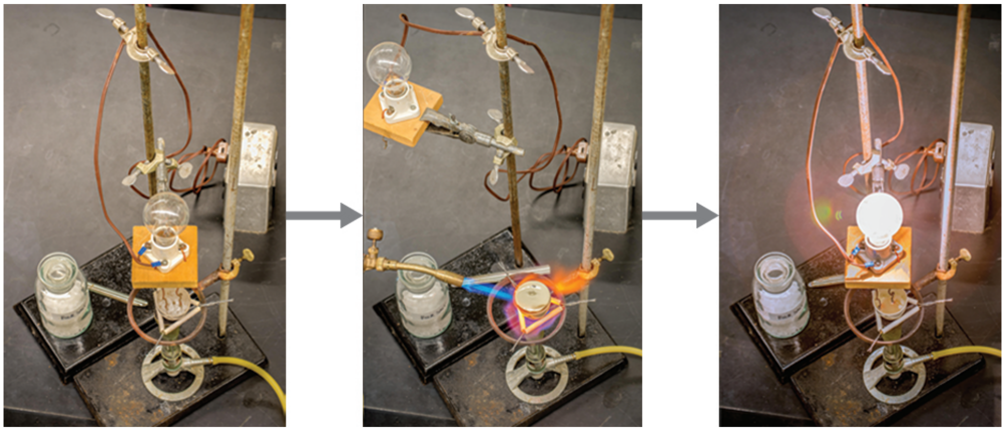

Figure 6.2a Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans in *Chemistry (OpenStax)*, CC BY 4.0).

Watch Conductivity Molten Salt Video (51 seconds)

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example 6.2a

Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

Exercise 6.2a

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Check Your Answer[1]

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 6.2a. **Oxyanions** are polyatomic ions that contain one or more oxygen atoms.

Table 6.2a Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	$NH_4{}^+$		
hydronium	H_3O^+		
oxide	$O_2{}^-$		
peroxide	$O_2{}^{2-}$		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	$N_3{}^-$	hydrazoic acid	HN_3
carbonate	$CO_3{}^{2-}$	carbonic acid	H_2CO_3
bicarbonate	$HCO_3{}^-$		
nitrate	$NO_3{}^-$	nitric acid	HNO_3
nitrite	$NO_2{}^-$	nitrous acid	HNO_2
sulfate	$SO_4{}^{2-}$	sulfuric acid	H_2SO_4
hydrogen sulfate	$HSO_4{}^-$		
sulfite	$SO_3{}^{2-}$	sulfurous acid	H_2SO_3
hydrogen sulfite	$HSO_3{}^-$		
phosphate	$PO_4{}^{3-}$	phosphoric acid	H_3PO_4
hydrogen phosphate	$HPO_4{}^{2-}$		
dihydrogen phosphate	$H_2PO_4{}^-$		
perchlorate	$ClO_4{}^-$	perchloric acid	$HClO_4$
chlorate	$ClO_3{}^-$	chloric acid	$HClO_3$
chlorite	$ClO_2{}^-$	chlorous acid	$HClO_2$

Name	Formula	Related Acid	Formula
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	${CrO_4}^{2-}$	chromic acid	H_2CrO_4
dichromate	${Cr_2O_7}^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	${MnO_4}^-$	permanganic acid	$HMnO_4$

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for “hyper”) and *hypo-* (meaning “under”) are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is $ClO_4{}^-$, chlorate is $ClO_3{}^-$, chlorite is $ClO_2{}^-$ and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is $NO_3{}^-$ while sulfate is $SO_4{}^{2-}$. This will be covered in more detail in the next module on nomenclature.

As you encounter monoatomic and polyatomic ions in different compounds and solutions, it is important to think about the differences in these ions. As was mentioned previously, monoatomic ions are simple in that these are formed when a single atom loses or gains a number of electrons. For example, a magnesium ion (Mg^{2+}) is formed when a magnesium atom loses two electrons. The atom that the ion is formed from as well as the charge of the ion is both represented in the formula.

Polyatomic ions are different in how we think about their formation and how we represent them. Polyatomic ions are still charged particles so we must represent the charge in the formula, but as the name implies these ions are formed from more than one atom. Let’s consider a sulfate ($SO_4{}^{2-}$) ion as our example as illustrated in Figure 6.2b. Using what we’ve learned in previous sections, we can see that there is one sulfur atom and four oxygen atoms and that there is a charge of -2. The sulfur atom is bonded to the oxygen atoms with covalent bonds. All five of those atoms bonded together make up the polyatomic ion.

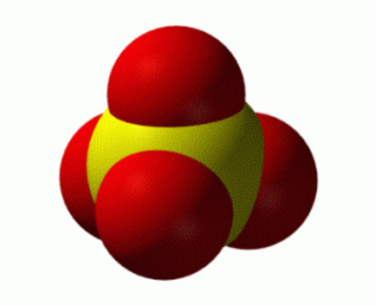

Figure 6.2b A space-filling image of a sulfate ion, where the S is represented by a yellow sphere and the oxygens are represented by red spheres. (credit: work by Benjah-bmm27, PD)

The 5-atom unit (1 x S, 4 x O) has an overall charge of -2. (It is incorrect to think that the oxygen has a -2 charge OR the sulfur has a -2 charge) In general, the atoms of a polyatomic ions (and the associated overall charge) stay together whether you are writing the ion by itself or as a part of a formula. This idea of keeping all of the atoms in a polyatomic together will be important when you learn about the dissociation of ionic compounds.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Example 6.2b

Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 6.2c) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?

Figure 6.2c Although pure aluminum oxide is colourless, trace amounts of iron and titanium give blue sapphire its characteristic colour. (credit: modification of work by Stanislav Doronenko, CC BY 3.0)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

Exercise 6.2b

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Check Your Answer[2]

Many ionic compounds contain polyatomic ions (Table 6.2a) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate (PO_4^{3-}) groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 6.2c

Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise 6.2c

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, O_2^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Check Your Answer[3]

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a **molecular formula**. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the **empirical formulas** introduced earlier in the book. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Attribution & References

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Notes

1. Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.
2. Na_2S
3. Li_2O_2

6.3 NAMING BINARY COMPOUNDS

Learning Objectives

By the end of this section, you will be able to:

- Generate a proper name for an ionic compound.
- Generate a proper name for a molecular compound

Nomenclature

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as **acids** (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principal element, will be introduced in a later chapter on organic chemistry.

Naming Binary Ionic Compounds

Naming ionic compounds is simple: combine the name of the cation and the name of the anion, in both cases omitting the word *ion*. *Do not use numerical prefixes if there is more than one ion necessary to balance the charges.* NaCl is sodium chloride, a combination of the name of the cation (sodium) and the anion (chloride). MgO is magnesium oxide. $MgCl_2$ is magnesium chloride—*not* magnesium dichloride.

In naming ionic compounds whose cations can have more than one possible charge, we must also include the charge, in parentheses and in roman numerals, as part of the name. Hence FeS is iron(II) sulfide, while

Fe_2S_3 is iron(III) sulfide. Again, no numerical prefixes appear in the name. The number of ions in the formula is dictated by the need to balance the positive and negative charges.

Example 6.3a

Problems

Name each ionic compound.

1. $CaCl_2$
2. AlF_3

Solutions

1. Using the names of the ions, this ionic compound is named calcium chloride. *It is not calcium(II) chloride* because calcium forms only one cation when it forms an ion, and it has a characteristic charge of 2+.
2. The name of this ionic compound is aluminum fluoride.

Exercise 6.3a

Name each ionic compound.

1. Sc_2O_3
2. AgCl

Check Your Answer[1]

Compounds Containing a Metal Ion with a Variable Charge

Most transition metals can form two or more cations with different charges.

There are two ways to make this distinction. In the simpler, more modern approach, called the **Stock**

system, an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word *ion*. Thus Fe^{2+} is called the iron(II) ion, while Fe^{3+} is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the Na^+ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Table 6.3a The Modern and Common System of Cation Names

Element	Stem	Charge	Modern Name	Common Name
iron	ferr-	2+	iron(II) ion	ferrous ion
iron	ferr-	3+	iron(III) ion	ferric ion
copper	cupr-	1+	copper(I) ion	cuprous ion
copper	cupr-	2+	copper(II) ion	cupric ion
tin	stann-	2+	tin(II) ion	stannous ion
tin	stann-	4+	tin(IV) ion	stannic ion
lead	plumb-	2+	lead(II) ion	plumbous ion
lead	plumb-	4+	lead(IV) ion	plumbic ion
chromium	chrom-	2+	chromium(II) ion	chromous ion
chromium	chrom-	3+	chromium(III) ion	chromic ion
gold	aur-	1+	gold(I) ion	aurous ion
gold	aur-	3+	gold(III) ion	auric ion

The second system, called the common system, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (-*ic* and –*ous*) that are appended to the stem of the element name. The -*ic* suffix represents the greater of the two cation charges, and the -*ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element.

Source: "3.4 Ionic Nomenclature" In *The Basics of General, Organic, and Biological Chemistry* by Saylor Academy, licensed under CC BY-NC-SA 3.0.

Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+, and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, "iron chloride," will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 6.3b.

Table 6.3b Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Table source: *General Chemistry 1 & 2* , a derivative of *Chemistry (Open Stax)*, CC BY 4.0

Out-of-date nomenclature used the suffixes –*ic* and –*ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example 6.3b

Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, Cl^{-}, and $SO_4{}^{2-}$), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{3+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. chromium(III) chloride
e. titanium(III) sulfate

Exercise 6.3b

Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. chromium(VI) fluoride

Check Your Answer[2]

Erin Brockovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.

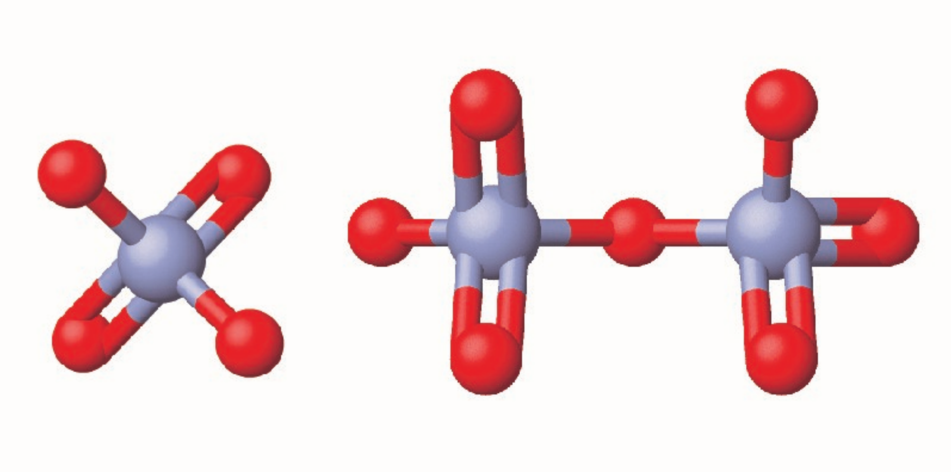

Figure 6.3a The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $Cr_2O_7^{2-}$ (right). (credit: *Chemistry (Open Stax)*, CC BY 4.0).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. But Cr(VI) is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Naming Molecular Compounds

How do you know whether a formula—and by extension, a name—is for a molecular compound or for an ionic compound? Molecular compounds form between nonmetals and nonmetals, while ionic compounds form between metals and nonmetals.

There are many substances that exist as two or more atoms connected together so strongly that they behave as a single particle. These multiatom combinations are called molecules. A molecule is the smallest part of a substance that has the physical and chemical properties of that substance. In some respects, a molecule is similar to an atom. A molecule, however, is composed of more than one atom.

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as diatomic molecules (Table 6.3c). As with any molecule, these elements are labeled with a molecular formula, a formal listing of what and how many atoms are in a molecule. (Sometimes only the word *formula* is used, and its meaning is inferred from the context.) For example, the molecular formula for elemental hydrogen is H_2, with H being the symbol for hydrogen and the subscript 2 implying that there are two atoms of this element in the molecule. Other diatomic elements have similar formulas: O_2, N_2, and so forth. Other elements exist as molecules—for example, sulfur normally exists as an eight-atom molecule, S_8, while phosphorus exists as a four-atom molecule, P_4 (see Figure 6.3b "Molecular Art of S"). Otherwise, we will assume that elements exist as individual atoms, rather than molecules. It is assumed that there is only one atom in a formula if there is no numerical subscript on the right side of an element's symbol.

Table 6.3c Elements that Exist as Diatomic Molecules

Name	Symbol
hydrogen	H_2
oxygen	O_2
nitrogen	N_2
fluorine	F_2
chlorine	Cl_2
bromine	Br_2
iodine	I_2

Table source: "Molecules and Chemical Nomenclature" In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, CC BY-NC-SA 4.0.

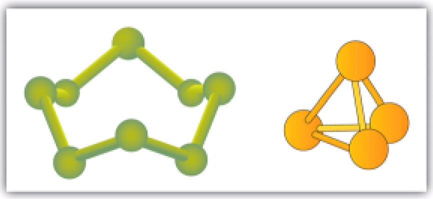

Figure 6.3b “Molecular Art of S_8 and P_4 Molecules.” If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule. (credit: Molecular Art of S_8 and P_4 Molecules by David W. Ball, CC BY-NC-SA 4.0)

Figure 6.3b “Molecular Art of S” shows two examples of how we will be representing molecules in this text. An atom is represented by a small ball or sphere, which generally indicates where the nucleus is in the molecule. A cylindrical line connecting the balls represents the connection between the atoms that make this collection of atoms a molecule. This connection is called a chemical bond.

Many compounds exist as molecules. In particular, when nonmetals connect with other nonmetals, the compound typically exists as molecules.

By following the rules of nomenclature, each and every compound has its own unique name, and each name refers to one and only one compound. Here, we will start with relatively simple molecules that have only two elements in them, the so-called *binary compounds*:

Step 1: Identify the elements in the molecule from its formula.

Step 2: Begin the name with the element name of the first element. If there is more than one atom of this element in the molecular formula, use a numerical prefix to indicate the number of atoms, as listed in Table 6.3c “Numerical Prefixes Used in Naming Molecular Compounds”. *Do not use the prefix* mono- *if there is only one atom of the first element.*

Table 6.3d Numerical Prefixes Used in Naming Molecular Compounds

Number of Atoms of Element	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

Step 3: Name the second element by using three pieces:

- a numerical prefix indicating the number of atoms of the second element, plus
- the stem of the element name (e.g., *ox* for oxygen, *chlor* for chlorine, etc.), plus
- the suffix *–ide*.

Step 4: Combine the two words, leaving a space between them.

The flowchart provides a summary for naming binary compounds (Figure 6.3c).

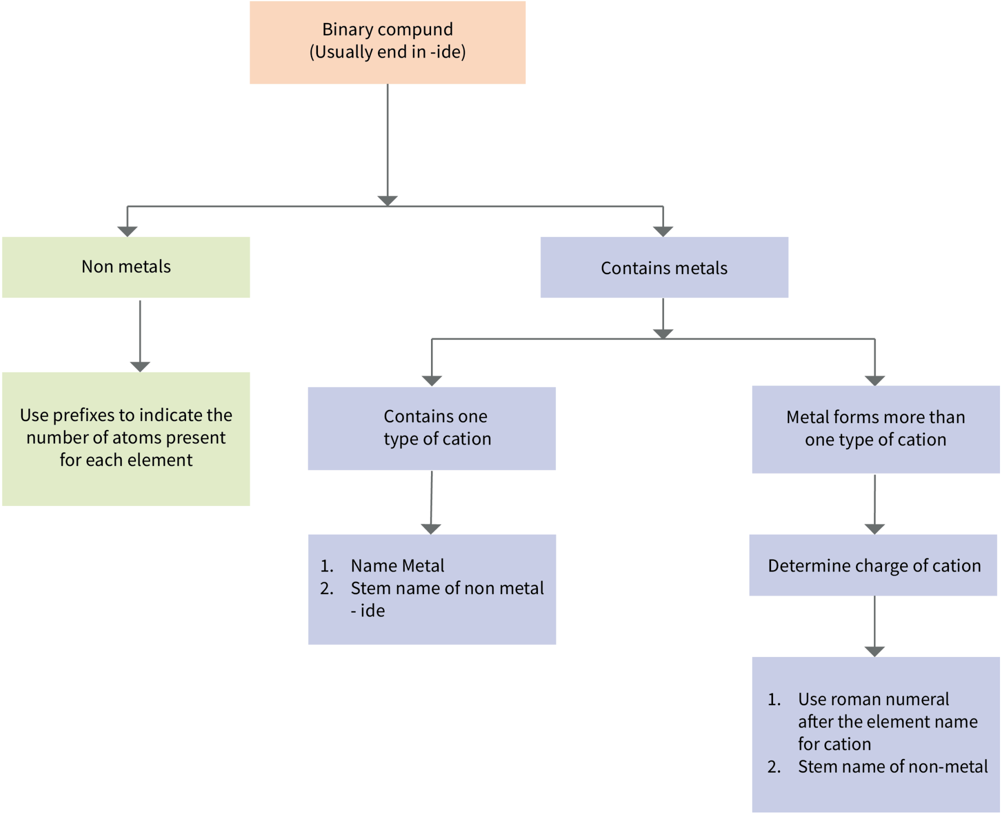

Figure 6.3c Flowchart for naming binary compounds. (credit: *Chemistry (Open Stax)*, CC BY 4.0. / Adapted into a flow chart by Revathi Mahadevan)

Let us see how these steps work for a molecule whose molecular formula is SO_2, which has one sulfur atom and two oxygen atoms—this completes step 1. According to step 2, we start with the name of the first element—sulfur. Remember, we don't use the *mono-* prefix for the first element. Now for step 3, we combine the numerical prefix *di-* (see Table 6.3c "Numerical Prefixes Used in Naming Molecular Compounds") with the stem *ox-* and the suffix *-ide*, to make *dioxide*. Bringing these two words together, we have the unique name for this compound—sulfur dioxide.

Why all this trouble? There is another common compound consisting of sulfur and oxygen whose molecular formula is SO_3, so the compounds need to be distinguished. SO_3 has three oxygen atoms in it, so it is a different compound with different chemical and physical properties. The system of chemical nomenclature is designed to *give this compound its own unique name*. Its name, if you go through all the steps, is sulfur trioxide. Different compounds have different names.

In some cases, when a prefix ends in *a* or *o* and the element name begins with *o* we drop the *a* or *o* on the prefix. So we see *monoxide* or *pentoxide* rather than *monooxide* or *pentaoxide* in molecule names.

One great thing about this system is that it works both ways. From the name of a compound, you should be able to determine its molecular formula. Simply list the element symbols, with a numerical subscript if there is more than one atom of that element, in the order of the name (we do not use a subscript 1 if there is only one atom of the element present; 1 is implied). From the name *nitrogen trichloride*, you should be able to get NCl_3 as the formula for this molecule. From the name *diphosphorus pentoxide*, you should be able to get the formula P_2O_5 (note the numerical prefix on the first element, indicating there is more than one atom of phosphorus in the formula).

Example 6.3c

Problems

Name each molecule.

1. PF_3
2. CO
3. Se_2Br_2

Solutions

1. A molecule with a single phosphorus atom and three fluorine atoms is called phosphorus trifluoride.
2. A compound with one carbon atom and one oxygen atom is properly called carbon monoxide, not carbon monooxide.
3. There are two atoms of each element, selenium and bromine. According to the rules, the proper name here is *diselenium dibromide.*

Exercise 6.3c

Name each molecule.

1. SF_4
2. P_2S_5

Check Your Answer[3]

Example 6.3d

Problems

Give the formula for each molecule.

1. carbon tetrachloride
2. silicon dioxide
3. trisilicon tetranitride

Solutions

1. The name carbon tetrachloride implies one carbon atom and four chlorine atoms, so the formula is CCl_4.
2. The name silicon dioxide implies one silicon atom and two oxygen atoms, so the formula is SiO_2.
3. We have a name that has numerical prefixes on both elements. Tri- means three, and tetra- means four, so the formula of this compound is Si_3N_4.

Exercise 6.3d

Give the formula for each molecule.

1. disulfur difluoride
2. iodine pentabromide

Check Your Answer[4]

Some simple molecules have common names that we use as part of the formal system of chemical nomenclature. For example, H_2O is given the name *water*, not *dihydrogen monoxide*. NH_3 is called *ammonia*, while CH_4 is called *methane*. We will occasionally see other molecules that have common names; we will point them out as they occur.

Links to Interactive Learning Tools

Practice Names to Formulas 1 by the Physics Classroom.

Explore Ion and Formula Writing from eCampusOntario H5P Studio.

Explore Naming Compounds Flow Chart from eCampusOntario H5P Studio.

Attribution & References

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- "Naming Molecular Compounds" section is adapted from Chapter 3: Ions and Ionic Compounds & Molecules and Chemical Nomenclature In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA 4.0.

Notes

1. 1. scandium oxide 2. silver chloride
2. (a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) CrF_6
3. 1. sulfur tetrafluoride; 2. diphosphorus pentasulfide
4. 1. S_2F_2; 2. IBr_5

6.4 NAMING COMPOUNDS CONTAINING POLYATOMIC IONS

Learning Objectives

By the end of this section, you will be able to:

- Generate a proper name for an ionic compound containing polyatomic ions.

Naming Compounds with Polyatomic ions

There also exists a group of ions that contain more than one atom. These are called polyatomic ions. Table 6.4a "Common Polyatomic Ions" lists the formulas, charges, and names of some common polyatomic ions. Only one of them, the ammonium ion, is a cation; the rest are anions. Most of them also contain oxygen atoms, so sometimes they are referred to as *oxyanions*. Some of them, such as nitrate and nitrite, and sulfate and sulfite, have very similar formulas and names, so care must be taken to get the formulas and names correct. Note that the -ite polyatomic ion has one less oxygen atom in its formula than the -ate ion but with the same ionic charge. For an accessible version of Table 6.4a, refer to Appendix E.

Table 6.4a Common Polyatomic Ions

Symbol	Name	Symbol	Name	Symbol	Name
CrO_4^{2-}	Chromate	BO_3^{3-}	Borate	SO_4^{2-}	Sulfate
CrO_7^{2-}	Dichromate	AsO_4^{3-}	Arsenate	SO_3^{2-}	Sulfite
CN^-	Cyanide	BrO^-	Hypobromite	HSO_4^-	Hydrogen sulfate (bisulfate)
SCN^-	Thiocyanide	BrO_3^-	Bromate	HSO_3^-	Hydrogen sulfite (bisulfate)
NO_3^-	Nitrate	CIO^-	Hypochlorite	PO_4^{3-}	Phosphate
NO_2^-	Nitrite	CIO_2^-	Chlorite	PO_3^{3-}	Phosphite
MnO_4^-	Permanganate	CIO_3^-	Chlorate	HPO_4^{2-}	Hydrogen phosphate
OH^-	Hydroxide	CIO_4^-	Perchlorate	$H_2PO_4^{2-}$	Dihydrogen phosphate
O_2^{2-}	Peroxide	IO_4^-	Periodate	CO_3^{2-}	Carbonate
NH_2^-	Amide	IO_3^-	Iodate	HCO_3^-	Hydrogen carbonate
$C_2H_3O_2^-$	Acetate	IO^-	Hypoiodite	$HC_2O_4^-$	Hydrogen oxalate
$C_2O_4^{2-}$	Oxalate	NH_4^+	Ammonium		

The naming of ionic compounds that contain polyatomic ions follows the same rules as the naming for other ionic compounds: simply combine the name of the cation and the name of the anion. Do not use numerical prefixes in the name if there is more than one polyatomic ion; the only exception to this is if the name of the ion itself contains a numerical prefix, such as dichromate or triiodide.

Writing the formulas of ionic compounds has one important difference. If more than one polyatomic ion is needed to balance the overall charge in the formula, enclose the formula of the polyatomic ion in parentheses and write the proper numerical subscript to the right and *outside* the parentheses. Thus, the formula between calcium ions, Ca^{2+}, and nitrate ions, NO_3^-, is properly written $Ca(NO_3)_2$, not $CaNO_{32}$ or CaN_2O_6. Use parentheses where required. The name of this ionic compound is simply calcium nitrate.

Example 6.4a

Problems

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

1. NH^{4+} and S^{2-}
2. Al^{3+} and PO_4^{3-}
3. Fe^{2+} and PO_4^{3-}

Solutions

1. Because the ammonium ion has a 1+ charge and the sulfide ion has a 2− charge, we need two ammonium ions to balance the charge on a single sulfide ion. Enclosing the formula for the ammonium ion in parentheses, we have $(NH_4)_2S$. The compound's name is ammonium sulfide.
2. Because the ions have the same magnitude of charge, we need only one of each to balance the charges. The formula is $AlPO_4$, and the name of the compound is aluminum phosphate.
3. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, we need three iron(II) ions, and to get 6−, we need two phosphate ions. The proper formula is $Fe_3(PO_4)_2$, and the compound's name is iron(II) phosphate.

Exercise 6.4a

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

1. NH_4^+ and PO_4^{3-}
2. Co^{3+} and NO_2^-

Check Your Answer[1]

Food and Drink App: Sodium in Your Food

The element sodium, at least in its ionic form as Na^+, is a necessary nutrient for humans to live. In fact, the human body is approximately 0.15% sodium, with the average person having one-twentieth to one-tenth of a kilogram in their body at any given time, mostly in fluids outside cells and in other bodily fluids.

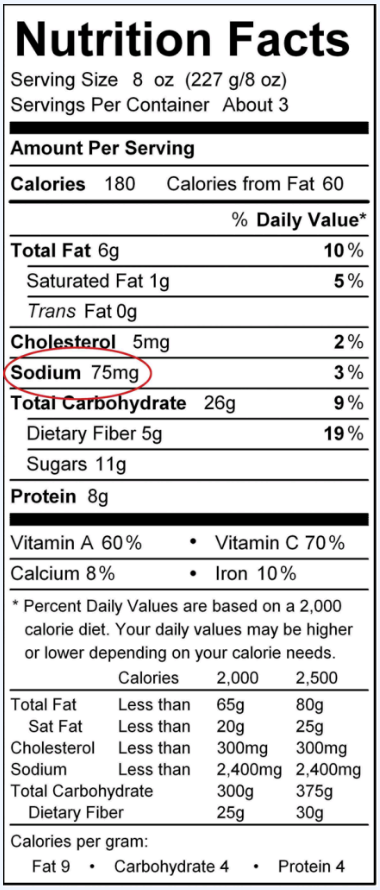
Sodium is also present in our diet. The common table salt we use on our foods is an ionic sodium compound. Many processed foods also contain significant amounts of sodium added to them as a variety of ionic compounds. Why are sodium compounds used so much? Usually sodium compounds are inexpensive, but, more importantly, most ionic sodium compounds dissolve easily. This allows processed food manufacturers to add sodium-containing substances to food mixtures and know that the compound will dissolve and distribute evenly throughout the food. Simple ionic compounds such as sodium nitrite ($NaNO_2$) are added to cured meats, such as bacon and deli-style meats, while a compound called sodium benzoate is added to many packaged foods as a preservative. Table 6.4b “Some Sodium Compounds Added to Food” is a partial list of some sodium additives used in food. Some of them you may recognize after reading this chapter. Others you may not recognize, but they are all ionic sodium compounds with some negatively charged ion also present.

Table 6.4b Some Sodium Compounds Added to Food

Sodium Compound	Use in Food
Sodium acetate	preservative, acidity regulator
Sodium adipate	food acid
Sodium alginate	thickener, vegetable gum, stabilizer, gelling agent, emulsifier
Sodium aluminum phosphate	acidity regulator, emulsifier
Sodium aluminosilicate	anticaking agent
Sodium ascorbate	antioxidant
Sodium benzoate	preservative
Sodium bicarbonate	mineral salt
Sodium bisulfite	preservative, antioxidant
Sodium carbonate	mineral salt
Sodium carboxymethylcellulose	emulsifier
Sodium citrates	food acid
Sodium dehydroacetate	preservative
Sodium erythorbate	antioxidant
Sodium erythorbin	antioxidant
Sodium ethyl para-hydroxybenzoate	preservative
Sodium ferrocyanide	anticaking agent
Sodium formate	preservative
Sodium fumarate	food acid
Sodium gluconate	stabilizer
Sodium hydrogen acetate	preservative, acidity regulator
Sodium hydroxide	mineral salt
Sodium lactate	food acid
Sodium malate	food acid
Sodium metabisulfite	preservative, antioxidant, bleaching agent
Sodium methyl para-hydroxybenzoate	preservative
Sodium nitrate	preservative, color fixative
Sodium nitrite	preservative, color fixative
Sodium orthophenyl phenol	preservative
Sodium propionate	preservative

Sodium Compound	Use in Food
Sodium propyl para-hydroxybenzoate	preservative
Sodium sorbate	preservative
Sodium stearoyl lactylate	emulsifier
Sodium succinates	acidity regulator, flavour enhancer
Sodium salts of fatty acids	emulsifier, stabilizer, anticaking agent
Sodium sulfite	mineral salt, preservative, antioxidant
Sodium sulfite	preservative, antioxidant
Sodium tartrate	food acid
Sodium tetraborate	preservative

The use of so many sodium compounds in prepared and processed foods has alarmed some physicians and nutritionists. They argue that the average person consumes too much sodium from his or her diet. The average person needs only about 500 mg of sodium every day; most people consume more than this—up to 10 times as much. Some studies have implicated increased sodium intake with high blood pressure; newer studies suggest that the link is questionable. However, there has been a push to reduce the amount of sodium most people ingest every day: avoid processed and manufactured foods, read labels on packaged foods (which include an indication of the sodium content), don't oversalt foods, and use other herbs and spices besides salt in cooking.



Nutrition Facts

Serving Size 8 oz (227 g/8 oz)
Servings Per Container About 3

Amount Per Serving

Calories 180 Calories from Fat 60

	% **Daily Value***
Total Fat 6g	**10** %
Saturated Fat 1g	**5** %
Trans Fat 0g	
Cholesterol 5mg	**2** %
Sodium 75mg	**3** %
Total Carbohydrate 26g	**9** %
Dietary Fiber 5g	**19** %
Sugars 11g	
Protein 8g	

Vitamin A 60% • Vitamin C 70%
Calcium 8% • Iron 10%

* Percent Daily Values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs.

	Calories	2,000	2,500
Total Fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2,400mg	2,400mg
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

Calories per gram:
Fat 9 • Carbohydrate 4 • Protein 4

Figure 6.4a "Nutrition Facts." Food labels include the amount of sodium per serving. This particular label shows that there are 75 mg of sodium in one serving of this particular food item (credit: *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, CC BY-NC-SA 4.0).

Indigenous Perspective: Soapstone

Explore two ionic compounds used by Inuit. These include stone such as soapstone (also known as talc carbonate) and composite materials such as bone which contains 70% hydroxyapatite, $Ca_5(PO_4)_3(OH)$.

The information can be found within the article Making Chemistry Relevant to Indigenous People [New Tab] from the University of Waterloo.

Figure 6.4b Soapstone (Speckstein) (credit: work by Ra'ike, CC BY-SA 3.0)

Source: Rayner-Canham, G., Taylor, R., & Lee, Y.R. (2016, February). Making chemistry relevant to Indigenous peoples. *Chem 13 News Magazine*. https://uwaterloo.ca/chem13-news-magazine/february-2016/feature/making-chemistry-relevant-indigenous-peoples

Links to Interactive Learning Tools

Practice Names to Formulas 2 by the Physics Classroom.

Explore Naming Compounds Flow Chart from eCampusOntario H5P Studio.

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Notes

1. 1. $(NH_4)_3PO_4$, ammonium phosphate

2. $Co(NO_2)_3$, cobalt(III) nitrite

6.5 NAMING ACIDS

Learning Objectives

By the end of this section, you will be able to:

- Define acid.
- Name a binary acid and an oxyacid.

There is one other group of compounds that is important to us—acids—and these compounds have interesting chemical properties. Initially, we will define an **acid** as an ionic compound of the H^+ cation dissolved in water. To indicate that something is dissolved in water, we will use the phase label (aq) next to a chemical formula (where aq stands for "aqueous," a word that describes something dissolved in water). If the formula does not have this label, then the compound is treated as a molecular compound rather than an acid.

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with acid is given a name derived from the compound's name. To indicate that something is dissolved in water, we will use the phrase label (aq) next to a chemical formula (where aq stands for "aqueous," a word that describes something dissolved in water). If the formula does not have this label, then the compound is treated as a molecular compound rather than an acid. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *–ic*
3. The word "acid" is added as a second word

A flowchart summarizes naming acids (Figure 6.5a).

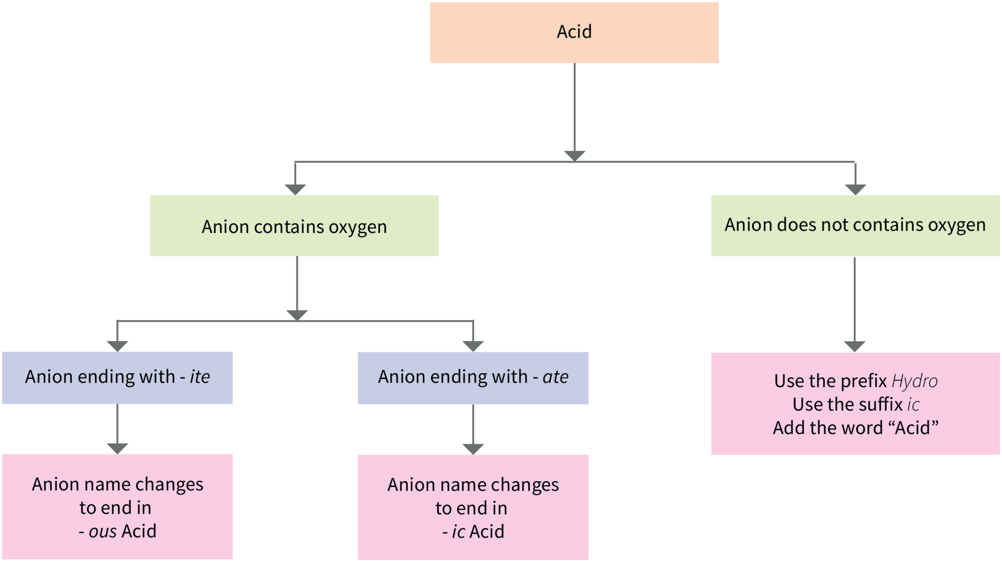

Figure 6.5a Flowchart for naming acids. (credit: *Chemistry (Open Stax)* CC BY 4.0. / Adapted into a flow chart by Revathi Mahadevan.)

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 6.5a.

Table 6.5a Names of Some Simple Acids

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as **oxyacids**, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit “hydrogen”
2. Start with the root name of the anion
3. Replace –*ate* with –*ic*, or –*ite* with –*ous*
4. Add “acid”

For example, consider H_2CO_3 (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the –*ate* of carbonate is replaced with –*ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 6.5b. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 6.5b Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Example 6.5a

Problems

Name each acid without consulting Table 6.6b.

1. HBr
2. H_2SO_4

Solutions

1. As a binary acid, the acid's name is *hydro-* + stem name + *-ic* acid. Because this acid contains a bromine atom, the name is hydrobromic acid.
2. Because this acid is derived from the sulfate ion, the name of the acid is the stem of the anion name + *-ic* acid. The name of this acid is sulfuric acid.

Exercise 6.5a

Name each acid.

1. HF
2. HNO_2

Check Your Answer[1]

All acids have some similar properties. For example, acids have a sour taste; in fact, the sour taste of some of our foods, such as citrus fruits and vinegar, is caused by the presence of acids in food. Many acids react with some metallic elements to form metal ions and elemental hydrogen. Acids make certain plant pigments change colours; indeed, the ripening of some fruits and vegetables is caused by the formation or destruction of excess acid in the plant. In a later chapter, we will explore the chemical behaviour of acids.

Acids are very prevalent in the world around us. We have already mentioned that citrus fruits contain acid; among other compounds, they contain citric acid, $H_3C_6H_5O_7(aq)$. Oxalic acid, $H_2C_2O_4(aq)$, is found in spinach and other green leafy vegetables. Hydrochloric acid not only is found in the stomach (stomach acid) but also can be bought in hardware stores as a cleaner for concrete and masonry. Phosphoric acid is an ingredient in some soft drinks.

Links to Interactive Learning Tools

Explore Naming Compounds Flow Chart from eCampusOntario H5P Studio.

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- "Chapter 3: Ions and Ionic Compounds & Molecules and Molecular Compounds – Acids" In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY NC SA 4.0. Access for free at *Chemistry 2e (OpenStax)*.

Adaptations include combining section 2.7, 4.3 and Chapter 3.

Notes

1.
    1. hydrofluoric acid
    2. nitrous acid

CHAPTER 6 - SUMMARY

6.1 Elements and Their Ions

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

6.2 Writing Formulas of Ionic Compounds

Ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. These compounds must be electrically neutral. For instance, NaCl would be electrically neutral since it has a single Na+ ion and a single Cl- ion.

6.3 Naming Binary Compounds

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride.

Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide.

6.4 Naming Compounds Containing Polyatomic Ions

Some compounds contain polyatomic ions. For compounds with polyatomic ions, name the metal first, followed by the name of the polyatomic ion.

6.5 Naming Acids

Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding “acid;” HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *–ic*, and adding “acid;” H_2CO_3 is carbonic acid.

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CHAPTER 6 - REVIEW

6.1 Elements and Their Ions

1. Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4. **Check Answer:** [1]
2. Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.
3. For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:
   1. NF_3
   2. BaO,
   3. $(NH_4)_2CO_3$
   4. $Sr(H_2PO_4)_2$
   5. IBr
   6. Na_2O

      Check Answer: [2]
4. For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:
   1. $KClO_4$
   2. $MgC_2H_3O_2$
   3. H_2S
   4. Ag_2S
   5. N_2Cl_4
   6. $Co(NO_3)_2$

6.2 Writing Formulas of Ionic Compounds; 6.3 Naming Binary Compounds; and 6.4 Naming Compounds Containing Polyatomic Ions

1. For each of the following pairs of ions, write the symbol for the formula of the compound they will form:
   1. Ca^{2+}, S^{2-}

- b. NH_4^+, SO_4^{2-}
- c. Al^{3+}, Br^-
- d. Na^+, HPO_4^{2-}
- e. Mg^{2+}, PO_4^{3-}

  Check Answer: [3]

2. For each of the following pairs of ions, write the symbol for the formula of the compound they will form:
   - a. K^+, O^{2-}
   - b. NH_4+, PO_4^{3-}
   - c. Al^{3+}, O^{2-}
   - d. Na^+, CO_3^{2-}
   - e. Ba^{2+}, PO_4^{3-}
3. Name the following compounds:
   - a. CsCl
   - b. BaO
   - c. K_2S
   - d. $BeCl_2$
   - e. HBr
   - f. AlF_3

   Check Answer: [4]
4. Name the following compounds:
   - a. NaF
   - b. Rb_2O
   - c. BCl_3
   - d. H_2Se
   - e. P_4O_6
   - f. ICl_3
5. Write the formulas of the following compounds:
   - a. rubidium bromide
   - b. magnesium selenide
   - c. sodium oxide
   - d. calcium chloride
   - e. hydrogen fluoride
   - f. gallium phosphide
   - g. aluminum bromide
   - h. ammonium sulfate

   Check Answer: [5]

6. Write the formulas of the following compounds:
    a. lithium carbonate
    b. sodium perchlorate
    c. barium hydroxide
    d. ammonium carbonate
    e. sulfuric acid
    f. calcium acetate
    g. magnesium phosphate
    h. sodium sulfite
7. Write the formulas of the following compounds:
    a. chlorine dioxide
    b. dinitrogen tetraoxide
    c. potassium phosphide
    d. silver(I) sulfide
    e. aluminum nitride
    f. silicon dioxide

    Check Answer: [6]
8. Write the formulas of the following compounds:
    a. barium chloride
    b. magnesium nitride
    c. sulfur dioxide
    d. nitrogen trichloride
    e. dinitrogen trioxide
    f. tin(IV) chloride
9. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:
    a. Cr_2O_3
    b. $FeCl_2$
    c. CrO_3
    d. $TiCl_4$
    e. CoO
    f. MoS_2

    Check Answer: [7]
10. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:
    a. $NiCO_3$
    b. MoO_3

    c. $Co(NO_3)_2$
    d. V_2O_5
    e. MnO_2
    f. Fe_2O_3
11. The following ionic compounds are found in common household products. Write the formulas for each compound:
    a. potassium phosphate
    b. copper(II) sulfate
    c. calcium chloride
    d. titanium dioxide
    e. ammonium nitrate
    f. sodium bisulfate (the common name for sodium hydrogen sulfate)

    Check Answer: [8]
12. The following ionic compounds are found in common household products. Name each of the compounds:
    a. $Ca(H_2PO_4)_2$
    b. $FeSO_4$
    c. $CaCO_3$
    d. MgO
    e. $NaNO_2$
    f. KI
13. What are the IUPAC names of the following compounds?
    a. manganese dioxide
    b. mercurous chloride (Hg_2Cl_2)
    c. ferric nitrate [$Fe(NO_3)_3$]
    d. titanium tetrachloride
    e. cupric bromide ($CuBr_2$)

    Check Answer: [9]

6.5 Naming Acids

1. Give the formula for each acid.
    a. perchloric acid
    b. hydriodic acid

    Check Answer: [10]
2. Give the formula for each acid.
    a. hydrosulfuric acid

    - b. phosphorous acid
3. Name each acid.
    - a. HF(aq)
    - b. HNO_3(aq)
    - c. $H_2C_2O_4$(aq)

    Check Answer: [11]
4. Name each acid.
    - a. H_2SO_4(aq)
    - b. H_3PO_4(aq)
    - c. HCl(aq)
5. Name an acid found in food.

    Check Answer: [12]
6. Name some properties that acids have in common.

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  Adaptations include extracting the exercises relevant to this chapter from 2.6, 2.7 and Chapter 3.

Notes

1. Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4
2. (a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, NH_4^{+},CO_3^{2-}; (d) ionic, Sr^{2+}, $H_2PO_4^{-}$; (e) covalent; (f) ionic, Na^{+}, O^{2-}
3. (a) CaS; (b) $(NH_4)_2SO_4$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3 (PO_4)_2$
4. (a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride
5. (a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$
6. (a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) AlN; (f) SiO_2
7. (a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) oxide; (f) molybdenum(IV) sulfide
8. (a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

9. (a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide
10. (a) $HClO_4(aq)$; (b) $HI(aq)$
11. (a) hydrofluoric acid; (b) nitric acid; (c) oxalic acid
12. Oxalic acid (answers will vary)

CHAPTER 7: A MOLE OF COMPOUNDS

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- Moles
- Avogadro's Number
- Molar Mass
- Numerical relationships between moles, mass and Avogadro's number

- The percent composition of compounds
- Deriving empirical and molecular formulas

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- The periodic table
- Elements
- Atomic Mass

Figure 7a The water in a swimming pool is a complex mixture of substances whose relative amounts must be carefully maintained to ensure the health and comfort of people using the pool. (credit: modification of work by Vic Brincat, CC BY 2.0)

Swimming pools have long been a popular means of recreation, exercise, and physical therapy. Since it is impractical to refill large pools with fresh water on a frequent basis, pool water is regularly treated with chemicals to prevent the growth of harmful bacteria and algae. Proper pool maintenance requires regular additions of various chemical compounds in carefully measured amounts. For example, the relative amount of calcium ion, Ca^{2+}, in the water should be maintained within certain limits to prevent eye irritation and avoid damage to the pool bed and plumbing. To maintain proper calcium levels, calcium cations are added to the water in the form of an ionic compound that also contains anions; thus, it is necessary to know both the relative amount of Ca^{2+} in the compound and the volume of water in the pool in order to achieve the proper calcium level. Quantitative aspects of the composition of substances (such as the calcium-containing compound) and mixtures (such as the pool water) are the subject of this chapter.

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7.1 THE MOLE CONCEPT AND AVOGADRO'S NUMBER

Learning Objectives

By the end of this section, you will be able to:

- Define the amount unit mole and the related quantity Avogadro's number
- Perform calculations between the mole and Avogadro's number

The identity of an elemental substance is defined not only by the type of atom it contains, but also by the quantity of atoms in the sample. For example, a 1.00 g sample of iron (Fe) contains 1.08 x 10^{22} atoms of iron. (That is a lot of atoms! If we were to divide those atoms up amongst each of the 7.9 billion people on earth in 2021, each person would have more than a trillion atoms). Because real samples we use in the laboratory will always be composed of very large numbers of atoms, scientists regularly use a unit, the **mole**, to count the very large quantities.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. By definition, a **mole** is the amount of a substance containing the same number of atoms as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word "mole" is "large mass" or "bulk," which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and the number of atoms present in a sample.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named **Avogadro's number (N_A)** or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. For atoms, this constant is properly reported with an explicit unit of "per mole," a conveniently rounded version being 6.022×10^{23} atoms/mol.

$$6.022 \text{ x } 10^{23} \text{ atoms} = 1 \text{ mole of atoms}$$

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The **molar mass** of an element is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see Figure 7.1a).

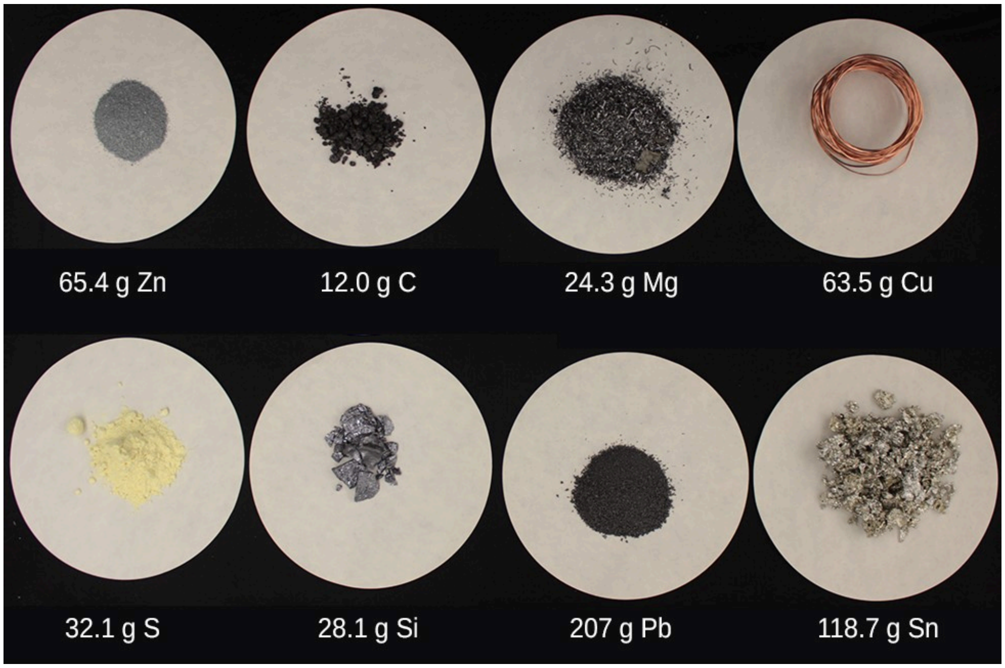

Figure 7.1a Each sample contains 6.022 × 10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. We can see this applied to several elements in Table 7.1a. While the numerical values are the same, the different units help us to remember whether we are describing the mass of a single atom or the mass of a very large number of atoms.

Table 7.1a Examples of elements and their mass in amu/atom and molar mass in g/mol.

Element	Mass of a single atom	Mass of 6.022 x 10^{23} atoms
argon (Ar)	39.95 amu/atom	39.95 g/mol
iron (Fe)	55.85 amu/atom	55.85 g/mol
selenium (Se)	78.96 amu/atom	78.96 g/mol

Watch How Big is a Mole (4:33 min)

The relationships atomic mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of an elemental substance. In this section, we will look at how the mole and Avogadro's Number can be related. The following expression can be used to express the relationship between the number of moles and Avogadro's Number:

$$\text{Number of atoms/molecules/ions} = n \times N_A$$

$N_A = 6.022 \times 10^{23}$ atoms/ions/molecules n = number of moles (mol)

Example 7.1a

How many atoms are in 3.5 moles of iron, Fe?

Approach

Convert the moles of Fe to the number of atoms using Avogadro's number.

Solution

Number of atoms = Amount of moles x Avogadro's number

Number of atoms = 3.5 mol x 6.022×10^{23} atoms/mol

Number of atoms = 2.1×10^{24} atoms of Fe

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Exercise 7.1a

How many atoms are present in 1.8 moles of Sodium, Na?

Check Your Answer[1]

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Example 7.1b

How many moles are present in 2.60 x 10^{21} atoms of Copper, Cu?

Approach

Convert the number of atoms to moles of Cu using Avogadro's number.

Solution

Amount of moles = Number of atoms / Avogadro's number

Amount of moles = 2.60 x 10^{21} atoms / 6.022 x 10^{23} atoms/mol

Amount of moles = 0.0043 moles of Cu

Source: "Example 7.1b" by Adrienne Richards is licensed under CC BY-NC 4.0.

Exercise 7.1b

How many moles are present in 1.80 x 10^{22} atoms of Silver, Ag?

Check Your Answer[2]

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Links to Interactive Learning Tools

Practice Mole Conversions by the Physics Classroom.

Key Equations

Number of atoms/molecules/ions = n x N_A

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Notes

1. 1.1 x 10^{24} atoms of Na
2. 0.030 moles

7.2 MOLECULAR MASS, AVOGADRO'S NUMBER AND THE MOLE

Learning Objectives

By the end of this section, you will be able to:

- Calculate molecular masses (or numerically equivalent molar masses) for covalent and ionic compounds
- Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving quantities from one another

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

Molecular Mass for Substances

The formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the **formula mass** may be correctly referred to as a molecular mass. This value of the formula mass can also be used to consider a substance's **molar mass** (numerically equivalent to molecular mass per 1 mole of substance as discussed in section 7.1). Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molar mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 7.2a outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu. The molecular mass of 119.37 amu expressed as a molar mass is 119.37 g/mol.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

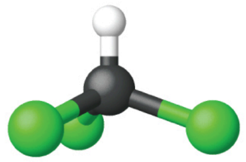


Figure 7.2a The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu (Figure 7.2b) or 180.15 g/mol (molar mass).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

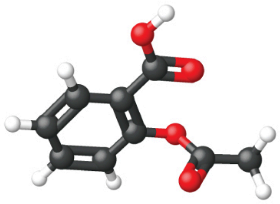


Figure 7.2b The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$ (credit: *Chemistry (OpenStax)*, CC BY 4.0).

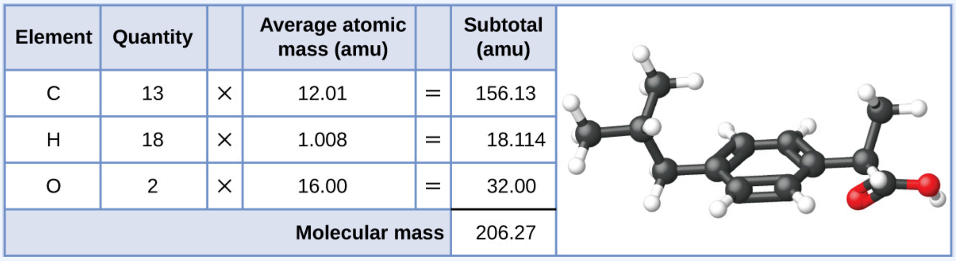
Example 7.2a

Computing Molecular Mass for a Covalent Compound

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound? What is the molar mass?

Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is, therefore:



Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
			Molecular mass		206.27

The molecular mass is 206.27 amu. The molar mass is 206.27 g/mol.

Exercise 7.2a

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound? What is the molar mass?

Check Your Answer[1]

Example 7.2b

Computing Molecular Mass for an Ionic Compound

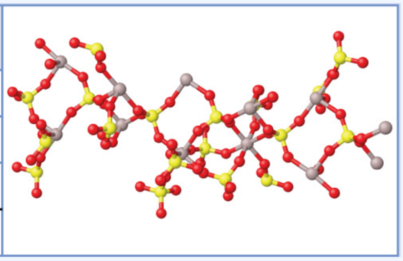
Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the molecular mass (amu) of this compound? What is the molar mass?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format,

$Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



The molecular mass is 342.14 amu. The molar mass is 342.14 g/mol.

Exercise 7.2b

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the molecular mass (amu) of calcium phosphate? What is the molar mass?

Check Your Answer[2]

The Mole

To review, the mole is an amount unit similar to familiar units like pair, dozen, gross, etc. In section 7.1, we learned it can be used to count atoms. The mole provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. It provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

Recall that Avogadro's number (N_A) is a constant and is properly reported with an explicit unit of "per mole." Therefore, we can use Avogadro's number for counting molecules as well:

$$6.022 \text{ x } 10^{23} \text{ molecules} = 1 \text{ mole of molecules}$$

Consistent with its definition as an amount unit, 1 mole of any compound contains the same number of molecules as 1 mole of any other compound. However, the molar mass of two different compounds will be different because their formula masses are different. The molar mass of a compound in grams is likewise *numerically* equivalent to its formula mass in amu (Figure 7.2c).

Figure 7.2c Each sample contains 6.02 × 10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa in *Chemistry (OpenStax)*, CC BY 4.0).

Table 7.2a Examples of elements average atomic mass, molar mass and atoms/mole.

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022 × 10^{23}
H	1.008	1.008	6.022 × 10^{23}
O	16.00	16.00	6.022 × 10^{23}
Na	22.99	22.99	6.022 × 10^{23}
Cl	35.45	33.45	6.022 × 10^{23}

While the formula mass and molar mass of a compound are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see Figure 7.2d). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.

Figure 7.2d The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: work by Tahlia Doyle, Unsplash license).

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate a number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

These relationships can be represented mathematically using the following expressions:

$$n = \frac{m}{M}$$

n = number of moles (mol) , m = mass (g) and M = molar mass (g/mol)

Number of atoms/ions/molecules = n x N_A

N_A = 6.022 x 10^{23} atoms/ions/molecules n = number of moles (mol)

Example 7.2c

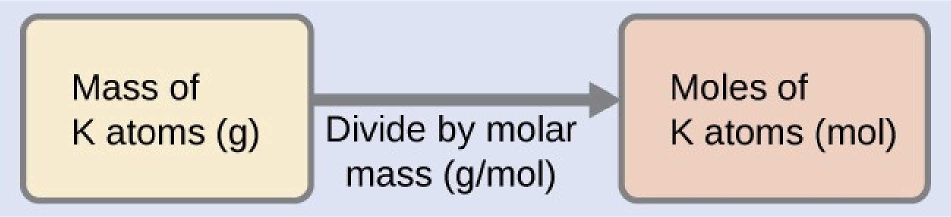
Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"

$$4.7\ \cancel{\text{g K}} \times \frac{1\ \text{mol K}}{39.10\ \cancel{\text{g K}}} = 0.12\ \text{mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

Exercise 7.2c

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Check Your Answer[3]

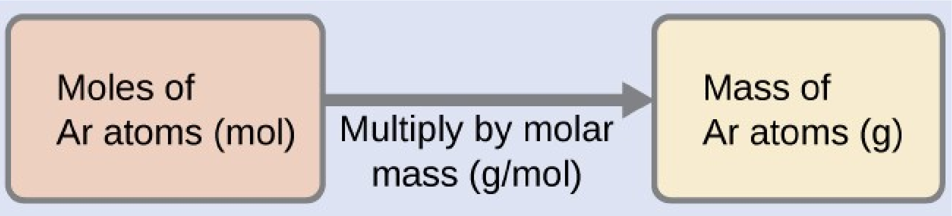
Example 7.2d

Deriving Grams from Moles for an Element

A litre of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a litre of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth ($\sim 10^{-3}$) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4}\ \cancel{\text{mol Ar}} \times \frac{39.95\text{ g Ar}}{1\ \cancel{\text{mol Ar}}} = 0.037\text{ g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

Exercise 7.2d

What is the mass of 2.561 mol of gold?

Check Your Answer[4]

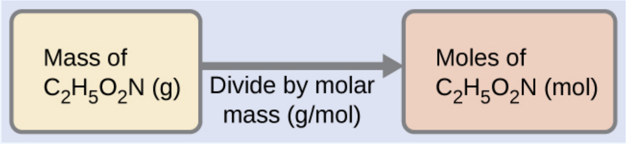
Example 7.2e

Deriving Moles from Grams for a Compound

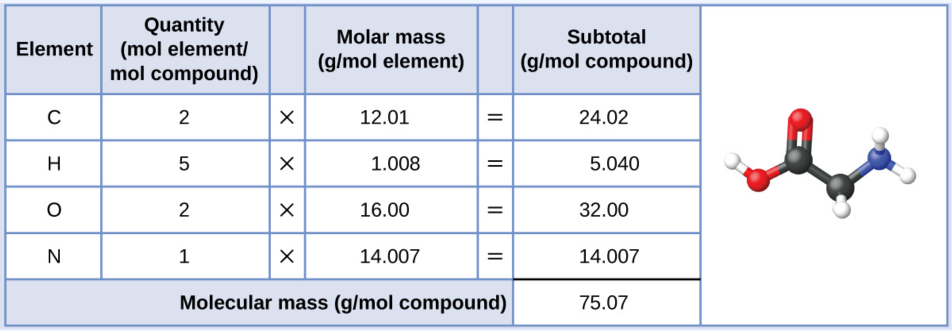
Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

Solution

We can derive the number of moles of a compound from its mass by the following:



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:



Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
			Molecular mass (g/mol compound)		75.07

The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

$$28.35\ \cancel{\text{g glycine}} \times \frac{1\ \text{mol glycine}}{75.07\ \cancel{\text{g glycine}}} = 0.378\ \text{mol glycine}$$

This result is consistent with our rough estimate.

Exercise 7.2e

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Check Your Answer[5]

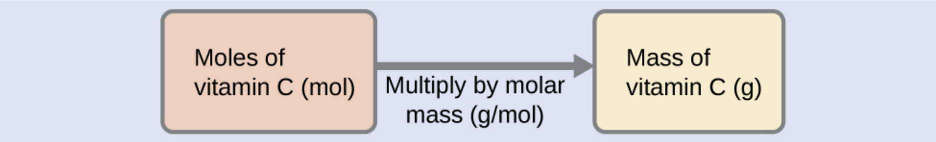
Example 7.2f

Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation, we get:

$$1.42 \times 10^{-4}\ \cancel{\text{mol vitamin C}} \times \frac{176.124\ \text{g vitamnin C}}{1\ \cancel{\text{mol vitamin C}}} = 0.0250\ \text{g vitamin C}$$

This is consistent with the anticipated result.

Exercise 7.2f

What is the mass of 0.443 mol of hydrazine, N_2H_4?

Check Your Answer[6]

Example 7.2g

Deriving the Number of Atoms from Mass for an Element

Copper is commonly used to fabricate electrical wire (Figure 7.2e). How many copper atoms are in 5.00 g of copper wire?

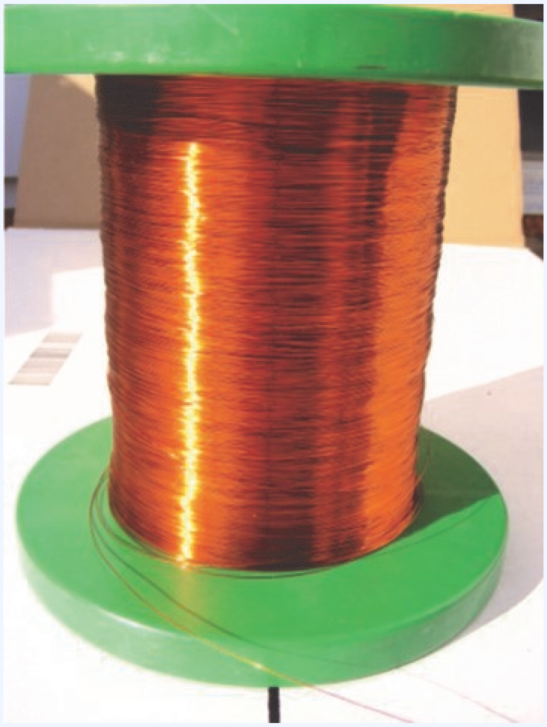
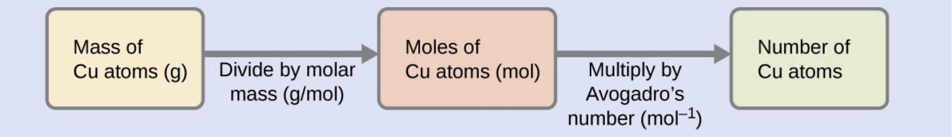


Figure 7.2e Copper wire is composed of many, many atoms of Cu. (credit: work by Emilian Robert Vicol, CC BY 2.0).

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (NA) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

$$5.00\ \cancel{\text{g Cu}} \times \frac{1\ \cancel{\text{mol Cu}}}{63.55\ \cancel{\text{g Cu}}} \times \frac{6.022 \times 10^{23}\ \text{atoms Cu}}{1\ \cancel{\text{mol Cu}}} = 4.74 \times 10^{22}\ \text{atoms Cu}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

Exercise 7.2g

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Check Your Answer[7]

Counting Neurotransmitter Molecules in the Brain

The brain is the control centre of the central nervous system (Figure 7.2f). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions; it processes stimuli detected by sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these advances through the concerted efforts of various industrial, academic, and government agencies.

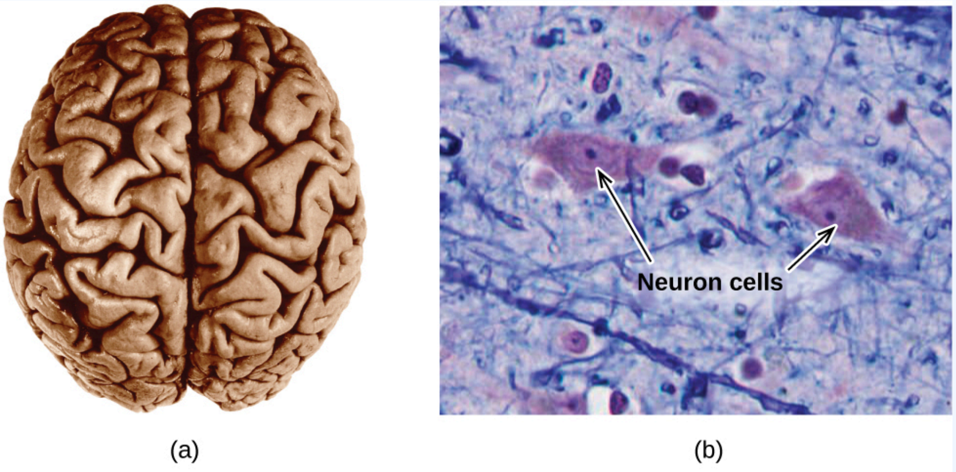


Figure 7.2f (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signalling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse) and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell wall and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see Figure 7.2g). One neurotransmitter that has been very extensively studied is dopamine, $C_8H_{11}NO_2$. Dopamine is involved in various neurological processes that impact a wide variety of human behaviours. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.

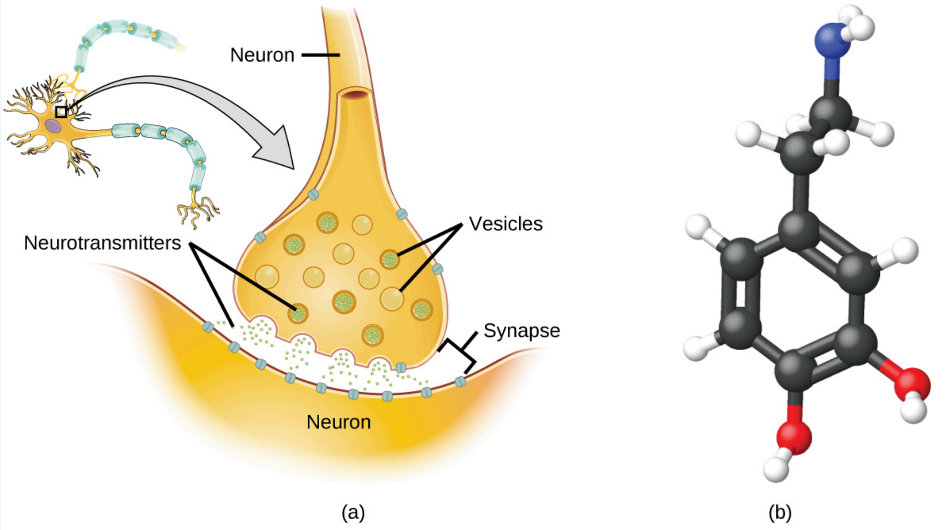


Figure 7.2g (a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine, $C_8H_{11}NO_2$, is a neurotransmitter involved in a number of neurological processes (credit: *Chemistry (OpenStax)*, CC BY 4.0).

One important aspect of the complex processes related to dopamine signalling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.

Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle (about 5×10^{-20} mol or 50 zmol). Analysis of these neurons from mice subjected to various drug therapies shows significant changes in the average number of dopamine molecules contained in individual vesicles, increasing or decreasing by up to three-fold, depending on the specific drug used. These studies also indicate that not all of the dopamine in a given vesicle is released during exocytosis, suggesting that it may be possible to regulate the fraction released using pharmaceutical therapies.[8]

Links to Interactive Learning Tools

Practice Molar Mass calculations from the Physics Classroom.

Practice Mole Conversions from the Physics Classroom.

Key Equations

$$n = \frac{m}{M}$$

Number of atoms/ions/molecules = n x N_A

Attribution & References

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- "6.1 Formula Mass and the Mole Concept" and "2.4 Counting Large Numbers of Atoms" In In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*
- "3.1 Formula Mass and the Mole Concept" In *Chemistry 2e (OpenStax)* by Paul Flowers, Klaus Theopold, Richard Langley, & William R. Robinson, licensed under CC BY 4.0. Access for free at *Chemistry 2e (OpenStax)*.

Notes

1. 151.16 amu ; 151.16 g/mol
2. 310.18 amu ; 310.18 g/mol
3. 0.360 mol Be
4. 504.4 g Ar
5. 0.073 mol $C_{12}H_{22}O_{11}$
6. 14.2 g hydrazine
7. 4.586×10^{22} Au atoms
8. Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

7.3 PERCENT COMPOSITION

Learning Objectives

By the end of this section, you will be able to:

- Compute the percent composition of a compound

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's **percent composition**, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%\ \text{H} = \frac{\text{mass H}}{\text{mass compound}} \times 100\%$$

$$\%\ \text{C} = \frac{\text{mass C}}{\text{mass compound}} \times 100\%$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\% \text{ H} = \frac{2.5 \text{ g H}}{10.0 \text{ g compound}} \times 100\% = 25\%$$
$$\% \text{ C} = \frac{7.5 \text{ g C}}{10.0 \text{ g compound}} \times 100\% = 75\%$$

Example 7.3a

Calculation of Percent Composition

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution

To calculate percent composition, we divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\% \text{ C} = \frac{7.34 \text{ g C}}{12.04 \text{ g compound}} \times 100\% = 61.0\%$$
$$\% \text{ H} = \frac{1.85 \text{ g H}}{12.04 \text{ g compound}} \times 100\% = 15.4\%$$
$$\% \text{ N} = \frac{2.85 \text{ g N}}{12.04 \text{ g compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

Exercise 7.3a

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

Check Your Answer[1]

Determining Percent Composition from Formula Mass

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea (CH_4N_2O). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for consumers choosing among these fertilizers. For these sorts of applications, the percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3 × 1.008 amu) = 3.024 amu. The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%\ \mathrm{N} = \frac{14.01\ \mathrm{amu\ N}}{17.03\ \mathrm{amu\ NH_3}} \times 100\% = 82.27\%$$

$$\%\ \mathrm{H} = \frac{3.024\ \mathrm{amu\ N}}{17.03\ \mathrm{amu\ NH_3}} \times 100\% = 17.76\%$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example 2. As long as we know the chemical formula of the substance in question, we can easily derive percent composition from the formula mass or molar mass.

Example 7.3b

Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula $C_9H_8O_4$. What is its percent composition?

Solution

To calculate the percent composition, we need to know the masses of C, H, and O in a known mass of $C_9H_8O_4$. It is convenient to consider 1 mol of $C_9H_8O_4$ and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\%\mathrm{C} \quad \frac{9\ \mathrm{mol\ C} \times \mathrm{molar\ mass\ C}}{\mathrm{molar\ mass\ C_9H_{18}O_4}} \times 100 = \frac{9{\times}12.01\ \mathrm{g/mol}}{180.159\mathrm{g/mol}} \times 100 = \frac{108.09\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100$$

$$\%\mathrm{C} \quad 60.00\%\ \mathrm{C}$$

$$\%\mathrm{H} \quad \frac{8\ \mathrm{mol\ H} \times \mathrm{molar\ mass\ H}}{\mathrm{molar\ mass\ C_9H_{18}O_4}} \times 100 = \frac{8{\times}1.008\ \mathrm{g/mol}}{180.159\mathrm{g/mol}} \times 100 = \frac{8.064\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100$$

$$\%\mathrm{H} \quad 4.476\%\ \mathrm{H}$$

$$\%\mathrm{O} \quad \frac{4\ \mathrm{mol\ O} \times \mathrm{molar\ mass\ O}}{\mathrm{molar\ mass\ C_9H_{18}O_4}} \times 100 = \frac{4{\times}16.00\ \mathrm{g/mol}}{180.159\mathrm{g/mol}} \times 100 = \frac{64.00\ \mathrm{g/mol}}{180.159\ \mathrm{g/mol}} \times 100$$

$$\%\mathrm{O} \quad 35.52\%\ \mathrm{O}$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

Exercise 7.3b

To three significant digits, what is the mass percentage of iron in the compound Fe_2O_3?

Check Your Answer[2]

Key Equations

- $\%\mathrm{X} = \dfrac{\mathrm{mass\ X}}{\mathrm{mass\ commpound}} \times 100\%$

Attribution & References

Except where otherwise noted, this page is adapted by Adrienne Richards from "6.2 Determining Empirical and Molecular Formulas" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*

Notes

1. 12.1% C, 16.1% O, 71.8% Cl
2. 69.9% Fe

7.4 DETERMINING EMPIRICAL AND MOLECULAR FORMULAS

Learning Objectives

By the end of this section, you will be able to:

- Determine the empirical formula of a compound
- Determine the molecular formula of a compound

Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, we must keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. To accomplish this, we can use molar masses to convert the mass of each element to a number of moles. We then consider the moles of each element relative to each other, converting these numbers into a whole-number ratio that can be used to derive the **empirical formula** of the substance. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$\begin{aligned} 1.17\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g C}} &= 0.142\text{ mol C} \\ 0.287\text{ g H} \times \frac{1\text{ mol H}}{1.008\text{ g H}} &= 0.284\text{ mol H} \end{aligned}$$

Thus, we can accurately represent this compound with the formula $C_{0.142}H_{0.248}$. Of course, per accepted convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$\mathrm{C}_{\frac{0.142}{0.142}}\ \mathrm{H}_{\frac{0.248}{0.142}}\ \text{or}\ \mathrm{CH_2}$$

(Recall that subscripts of "1" are not written but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2. This may or not be the compound's **molecular formula** as well; however, we would need additional information to make that determination (as discussed later in this section).

A molecular formula is the true formula for a compound. It lists how many atoms of each element are in the compound. The empirical formula is the simplest or most reduced ratio of elements in a compound. If a compound's chemical formula cannot be reduced any further, then the empirical formula is the same as the molecular formula.

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$\mathrm{Cl_{0.150}O_{0.525}} = \mathrm{Cl}_{\frac{0.150}{0.150}}\ \mathrm{O}_{\frac{0.525}{0.150}} = \mathrm{ClO_{3.5}}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, we must multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure 7.4a outlines this procedure in flow chart fashion for a substance containing elements A and X.

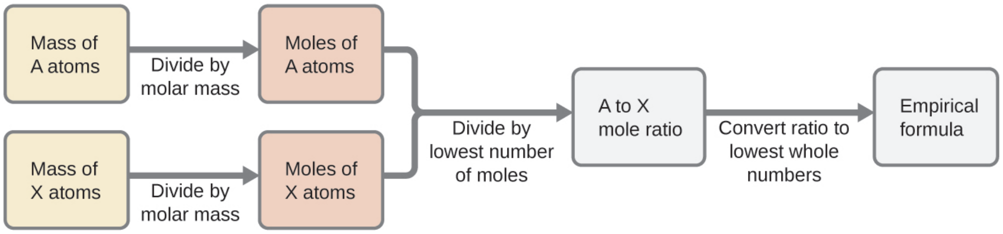

Figure 7.4a The empirical formula of a compound can be derived from the masses of all elements in the sample (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 7.4a

Determining a Compound’s Empirical Formula from the Masses of Its Elements

A sample of the black mineral hematite (Figure 7.3b), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?

Figure 7.4b Hematite is an iron oxide that is used in jewelry. (credit: work by Mauro Cateb, CC BY-SA 3.0)

Solution

For this problem, we are given the mass in grams of each element. Begin by finding the moles of each:

$$34.97\text{ g Fe}\left(\frac{\text{mol Fe}}{55.85\text{ g}}\right)\quad 0.6261\text{ mol Fe}$$

$$15.03\text{ g O}\left(\frac{\text{mol O}}{16.00\text{ g}}\right)\quad 0.9394\text{ mol O}$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261}\quad 1.000\text{ mol Fe}$$

$$\frac{0.9394}{0.6261}\quad 1.500\text{ mol O}$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

$$2(\text{Fe}_1\text{O}_{1.5}) = \text{Fe}_2\text{O}_3$$

The empirical formula is Fe_2O_3.

Exercise 7.4a

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Check Your Answer[1]

Watch Calculating Percent Composition and Empirical Formulas

Deriving Empirical Formulas from Percent Composition

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

Example 7.4b

Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O (Figure 7.3c). What is the empirical formula for this gas?

Figure 7.4c An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: work by Dual Freq, CC BY-SA 3.0)

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is “most convenient” because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element’s mass percentage. This numerical equivalence results from the definition of the “percentage” unit, whose name is derived from the Latin phrase *per centum* meaning “by the hundred.” Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\%\ \text{C} \quad \frac{27.29\ \text{g C}}{100\ \text{g compound}}$$

$$72.71\%\ \text{O} \quad \frac{72.71\ \text{g O}}{100\ \text{g compound}}$$

The molar amounts of carbon and hydrogen in a 100-g sample are calculated by dividing each element’s mass by its molar mass:

$$27.29\%\ \mathrm{C}\left(\frac{\mathrm{mol\ C}}{12.01\ \mathrm{g}}\right)\quad 2.272\ \mathrm{mol\ C}$$

$$72.71\%\ \mathrm{O}\left(\frac{\mathrm{mol\ O}}{16.00\ \mathrm{g}}\right)\quad 4.544\ \mathrm{mol\ O}$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272\ \mathrm{g\ C}}{2.272}\quad 1$$

$$\frac{4.544\ \mathrm{g\ O}}{2.272}\quad 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

Exercise 7.4b

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

Check Your Answer[2]

Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its **empirical formula mass**. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule, which we designate as *n*:

$$\frac{\text{molecular or molar mass (amu or } \frac{\text{g}}{\text{mol}})}{\text{empirical formula mass (amu or } \frac{\text{g}}{\text{mol}})} = n \text{ formula units/molecule}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by *n*, as shown by the generic empirical formula A_xB_y:

$$(A_xB_y)_n = A_{nx}B_{nx}$$

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180 \text{ amu/molecule}}{30 \ \frac{\text{amu}}{\text{formula unit}}} = 6 \text{ formula units/molecule}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(CH_2O)_6 = C_6H_{12}O_6$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

Example 7.4c

Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02 \text{ g C})(\frac{1 \text{ mol C}}{12.01 \text{ g C}}) \quad 6.163 \text{ mol C}$$

$$(8.710 \text{ g H})(\frac{1 \text{ mol H}}{1.01 \text{ g H}}) \quad 8.624 \text{ mol H}$$

$$(17.27 \text{ g N})(\frac{1 \text{ mol N}}{14.01 \text{ g N}}) \quad 1.233 \text{ mol N}$$

Next, we calculate the molar ratios of these elements relative to the least abundant element, N.

$$6.163 \text{ mol C}/1.233 \text{ mol N} \quad 5$$

$$8.264 \text{ mol H}/1.233 \text{ mol N} \quad 7$$

$$1.233 \text{ mol N}/1.233 \text{ mol N} \quad 1$$

$$\frac{1.233}{1.233} \quad 1.000 \text{ mol N}$$

$$\frac{6.163}{1.233} \quad 4.998 \text{ mol C}$$

$$\frac{8.624}{1.233} \quad 6.994 \text{ mol H}$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

We calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57 \text{ g nicotine}}{0.2500 \text{ mol nicotine}} = \frac{162.3 \text{ g}}{\text{mol}}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3 \text{ g/mol}}{81.13 \ \frac{\text{g}}{\text{formula unit}}} = 2 \text{ formula units/molecule}$$

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2$$

Exercise 7.4c

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Check Your Answer[3]

Glucose, an example of empirical vs molecular formulas

Consider glucose, the sugar that circulates in our blood to provide fuel for the body and brain. Results from combustion analysis of glucose report that glucose contains 39.68% carbon and 6.58% hydrogen. Because combustion occurs in the presence of oxygen, it is impossible to directly determine the percentage of oxygen in a compound by using combustion analysis; other more complex methods are necessary. Assuming that the remaining percentage is due to oxygen, then glucose would contain 53.79% oxygen. A 100.0 g sample of glucose would therefore contain 39.68 g of carbon, 6.58 g of hydrogen, and 53.79 g of oxygen. To calculate the number of moles of each element in the 100.0 g sample, divide the mass of each element by its molar mass:

$$moles\,C = 39.68\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 3.304\,mol\,C$$

$$moles\,H = 6.58\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 6.53\,mol\,H$$

$$moles\,O = 53.79\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 3.362\,mol\,O$$

Once again, the subscripts of the elements in the empirical formula are found by dividing the number of moles of each element by the number of moles of the element present in the smallest amount:

$$C : \frac{3.304}{3.304} = 1.000 \quad H : \frac{6.53}{3.304} = 1.98 \quad O : \frac{3.362}{3.304} = 1.018$$

The oxygen:carbon ratio is 1.018, or approximately 1, and the hydrogen:carbon ratio is approximately 2. The empirical formula of glucose is therefore CH_2O, but what is its molecular formula?

Many known compounds have the empirical formula CH_2O, including formaldehyde, which is used to preserve biological specimens and has properties that are very different from the sugar circulating in the blood. At this point, it cannot be known whether glucose is CH_2O, $C_2H_4O_2$, or any other $(CH_2O)_n$. However, the experimentally determined molar mass of glucose (180 g/mol) can be used to resolve this dilemma.

First, calculate the formula mass, the molar mass of the formula unit, which is the sum of the atomic masses of the elements in the empirical formula multiplied by their respective subscripts. For glucose,

$$\text{formula mass of} CH_2O = \left[1\,mol C\left(\frac{12.011\,g}{1\,mol\,C}\right)\right] + \left[2\,mol\,H\left(\frac{1.0079\,g}{1\,mol\,H}\right)\right] + \left[1\,mole\,O\left(\frac{15.5994\,mol\,O}{1\,mol\,O}\right)\right] = 30.026g$$

This is much smaller than the observed molar mass of 180 g/mol.

Second, determine the number of formula units per mole. For glucose, calculate the number of (CH_2O) units—that is, the n in $(CH_2O)_n$—by dividing the molar mass of glucose by the formula mass of CH_2O:

$$n = \frac{180\,g}{30.026\,g/CH_2O} = 5.99 \approx 6CH_2O\,\textbf{formula units}$$

Each glucose contains six CH_2O formula units, which gives a molecular formula for glucose of $(CH_2O)_6$, which is more commonly written as $C_6H_{12}O_6$. The molecular structures of formaldehyde and glucose, both of which have the empirical formula CH_2O, are shown in Figure 7.4d:

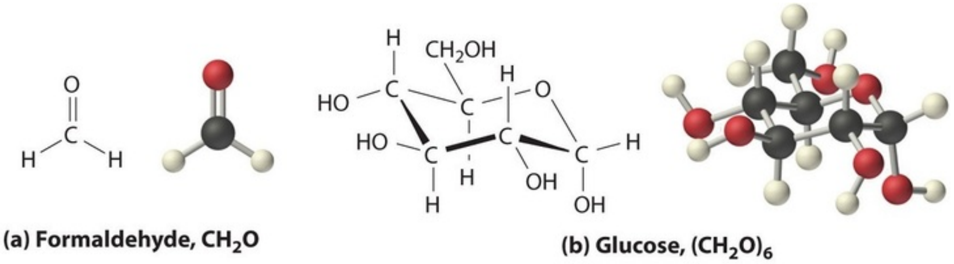

Figure 7.4d Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose

Source: "Glucose, an example of empirical vs molecular formulas" is adapted from "Empirical and Molecular Formulas" In *Chemistry 101A (LibreTexts)*, licensed under CC BY-NC-SA 4.0.

Scientists in Action: Ellen Henrietta Swallow Richards, PhD.

Figure 7.4e Ore containing copper, cobalt, and nickel (credit: work by Paul-Alain Hunt, Unsplash license)

Ellen Henrietta Swallow Richards spent much of her career studying the quantity of substances within compounds whether it was in water, metals or food. She was able to determine the amount of nickel in various ores and the relative quantities of substances in food and water. Her work led to educating the population on nutrition from foods, clean water standards and how to chemically analyze ores.

Read more about Ellen's history and contributions to chemistry provided by the American Society of Civil Engineers [New Tab].

Key Equations

- $\%\text{X} = \dfrac{\text{mass X}}{\text{mass commpound}} \times 100\%$
- $\dfrac{\text{molecular or molar mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)} = n\text{ formula units/molecule}$
- $(\text{A}_x\text{B}_y)_n = \text{A}_{nx}\text{B}_{ny}$

Attribution & References

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Notes

1. N_2O_5
2. CH_2O
3. $C_8H_{10}N_4O_2$

CHAPTER 7 SUMMARY

7.1 The Mole Concept & Avogadro's Number

A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be 6.022×10^{23}, a quantity called Avogadro's number.

7.2 Molecular Mass, Avogadro's Number and The Mole

The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called molecular mass.

The mass in grams of 1 mole of a substance is its molar mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately 18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

7.3 Percent Composition

The percent composition is the percentage by mass of each element in the compound. The percent composition of each element in a compound can be used to determine the empirical and molecular formulas of the compound.

7.4 Determining the Empirical and Molecular Formulas

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

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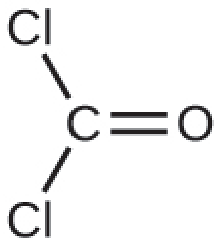
CHAPTER 7 - REVIEW

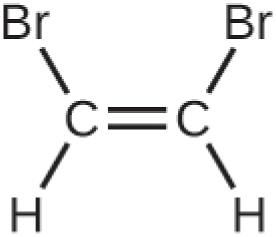
7.1 The Mole Concept and Avogadro's Number; and 7.2 Molecular Mass, Avogadro's Number and The Mole

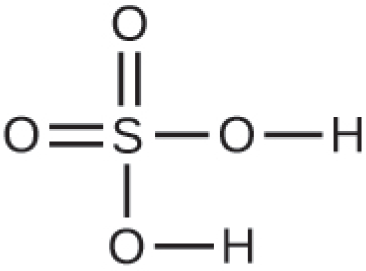
1. What is the total mass (amu and g/mol) of carbon in each of the following molecules?
    a. CH_4
    b. $CHCl_3$
    c. $C_{12}H_{10}O_6$
    d. $CH_3CH_2CH_2CH_2CH_3$
    Check Answer: [1]
2. What is the total mass (amu and g/mol) of hydrogen in each of the molecules?
    a. CH_4
    b. $CHCl_3$
    c. $C_{12}H_{10}O_6$
    d. $CH_3CH_2CH_2CH_2CH_3$
3. Calculate the molecular or formula mass and molar mass of each of the following:
    a. P_4
    b. H_2O
    c. $Ca(NO_3)_2$
    d. CH_3CO_2H (acetic acid)
    e. $C_{12}H_{22}O_{11}$ (sucrose, cane sugar).
    Check Answer: [2]
4. Determine the molecular mass and molar mass of the following compounds:

(a)

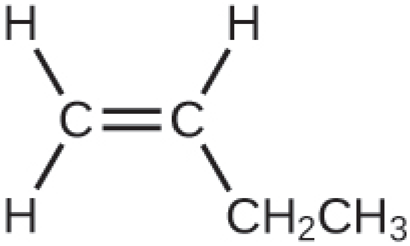


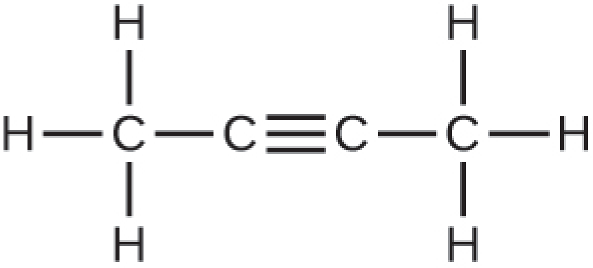
(b)

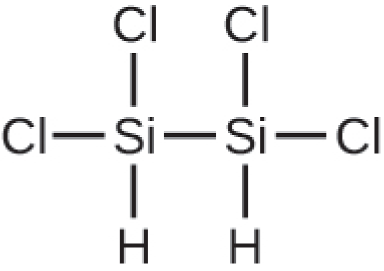
(c) 

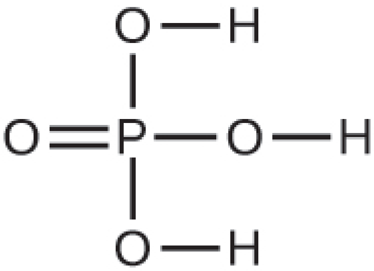
(d) 

5. Determine the molecular mass and molar mass of the following compounds: **Check Answer:** [3]

(a) 

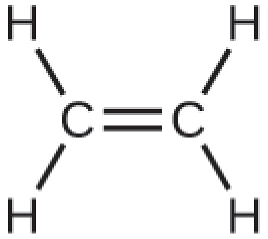
(b) 

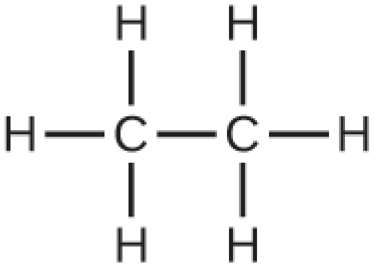
(c) 

(d) 

6. Which molecule has a molecular mass of 28.05 amu?

(a) 

(b) 

(c) 

7. Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula. **Check Answer:** [4]
8. Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.
   a. Which has the largest number of molecules? Explain why.
   b. Which has the greatest mass? Explain why.
9. Which contains the greatest mass of oxygen: 0.75 mol of ethanol (C_2H_5OH), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why. **Check Answer:** [5]
10. Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol (C_2H_5OH), 1 mol of formic acid (HCO_2H), or 1 mol of water (H_2O)? Explain why.
11. How are the molecular mass and the molar mass of a compound similar and how are they different? **Check Answer:** [6]
12. Calculate the molar mass of each of the following compounds:
    a. hydrogen fluoride, HF
    b. ammonia, NH_3
    c. nitric acid, HNO_3
    d. silver sulfate, Ag_2SO_4
    e. boric acid, $B(OH)_3$
13. Calculate the molar mass of each of the following:
    a. S_8
    b. C_5H_{12}
    c. $Sc_2(SO_4)_3$
    d. CH_3COCH_3 (acetone)
    e. $C_6H_{12}O_6$ (glucose)
    Check Answer: [7]
14. Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

   a. limestone, $CaCO_3$
   b. halite, NaCl
   c. beryl, $Be_3Al_2Si_6O_{18}$
   d. malachite, $Cu_2(OH)_2CO_3$
   e. turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$
15. Calculate the molar mass of each of the following:
   a. the anesthetic halothane, $C_2HBrClF_3$
   b. the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$
   c. caffeine, $C_8H_{10}N_4O_2$
   d. urea, $CO(NH_2)_2$
   e. a typical soap, $C_{17}H_{35}CO_2Na$

   Check Answer: [8]
16. Determine the number of moles of compound and the number of moles of each type of atom in each of the following:
   a. 25.0 g of propylene, C_3H_6
   b. 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$
   c. 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)
   d. 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$
   e. 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$
17. Determine the mass of each of the following:
   a. 0.0146 mol KOH
   b. 10.2 mol ethane, C_2H_6
   c. 1.6×10^{-3} mol Na_2SO_4
   d. 6.854×10^{3} mol glucose, $C_6H_{12}O_6$
   e. 2.86 mol $Co(NH_3)_6Cl_3$

   Check Answer: [9]
18. Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:
   a. 2.12 g of potassium bromide, KBr
   b. 0.1488 g of phosphoric acid, H_3PO_4
   c. 23 kg of calcium carbonate, $CaCO_3$
   d. 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$
   e. 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$
19. Determine the mass of each of the following:
   a. 2.345 mol LiCl
   b. 0.0872 mol acetylene, C_2H_2
   c. 3.3×10^{-2} mol Na_2CO_3

   d. 1.23×10^3 mol fructose, $C_6H_{12}O_6$
   e. 0.5758 mol $FeSO_4(H_2O)_7$
   Check Answer: [10]
20. The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, is 1.1 g. What is this requirement in moles?
21. Determine the mass in grams of each of the following:
   a. 0.600 mol of oxygen atoms
   b. 0.600 mol of oxygen molecules, O_2
   c. 0.600 mol of ozone molecules, O_3
   Check Answer: [11]
22. A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?
23. Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon, $ZrSiO_4$, a semiprecious stone. **Check Answer:** [12]
24. Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4, 0.6 mol of C_6H_6, or 0.4 mol of C_3H_8.
25. Determine which of the following contains the greatest mass of aluminum: 122 g of $AlPO_4$, 266 g of Al_2C1_6, or 225 g of Al_2S_3. **Check Answer:** [13]
26. Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?
27. The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone? **Check Answer:** [14]
28. One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?
29. A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar? **Check Answer:** [15]
30. A tube of toothpaste contains 0.76 g of sodium monofluorophosphate (Na_2PO_3F) in 100 mL.
   a. What mass of fluorine atoms in mg was present?
   b. How many fluorine atoms were present?
31. Which of the following represents the least number of molecules?
   a. 20.0 g of H_2O (18.02 g/mol)
   b. 77.0 g of CH_4 (16.06 g/mol)
   c. 68.0 g of CaH_2 (42.09 g/mol)
   d. 100.0 g of N_2O (44.02 g/mol)
   e. 84.0 g of HF (20.01 g/mol)
   Check Answer: [16]

7.3 Percent Composition; and 7.4 Determining Empirical and Molecular Formulas

1. What information do we need to determine the molecular formula of a compound from the empirical formula?
2. Calculate the following to four significant figures:
   a. the percent composition of ammonia, NH_3
   b. the percent composition of photographic “hypo,” $Na_2S_2O_3$
   c. the percent of calcium ion in $Ca_3(PO_4)_2$
   Check Answer: [17]
3. Determine the following to four significant figures:
   a. the percent composition of hydrazoic acid, HN_3
   b. the percent composition of TNT, $C_6H_2(CH_3)(NO_2)_3$
   c. the percent of $SO_4{}^{2-}$ in $Al_2(SO_4)_3$
4. Determine the percent ammonia, NH_3, in $Co(NH_3)_6Cl_3$, to three significant figures. **Check Answer:** [18]
5. Determine the percent water in $CuSO_4{\cdot}5H_2O$ to three significant figures.
6. Determine the empirical formulas for compounds with the following percent compositions:
   a. 15.8% carbon and 84.2% sulfur
   b. 40.0% carbon, 6.7% hydrogen, and 53.3% oxygen
   Check Answer: [19]
7. Determine the empirical formulas for compounds with the following percent compositions:
   a. 43.6% phosphorus and 56.4% oxygen
   b. 28.7% K, 1.5% H, 22.8% P, and 47.0% O
8. A compound of carbon and hydrogen contains 92.3% C and has a molar mass of 78.1 g/mol. What is its molecular formula? **Check Answer:** [20]
9. Dichloroethane, a compound that is often used for dry cleaning, contains carbon, hydrogen, and chlorine. It has a molar mass of 99 g/mol. Analysis of a sample shows that it contains 24.3% carbon and 4.1% hydrogen. What is its molecular formula?
10. Determine the empirical and molecular formula for chrysotile asbestos. Chrysotile has the following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O. The molar mass for chrysotile is 520.8 g/mol. **Check Answer:** [21]
11. Polymers are large molecules composed of simple units repeated many times. Thus, they often have relatively simple empirical formulas. Calculate the empirical formulas of the following polymers:
    a. Lucite (Plexiglas); 59.9% C, 8.06% H, 32.0% O
    b. Saran; 24.8% C, 2.0% H, 73.1% Cl
    c. polyethylene; 86% C, 14% H

   d. polystyrene; 92.3% C, 7.7% H
   e. Orlon; 67.9% C, 5.70% H, 26.4% N

12. A major textile dye manufacturer developed a new yellow dye. The dye has a percent composition of 75.95% C, 17.72% N, and 6.33% H by mass with a molar mass of about 240 g/mol. Determine the molecular formula of the dye. **Check Answer:** [22]

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Notes

1. (a) 12.01 amu or g/mol; (b) 12.01 amu or g/mol; (c) 144.12 amu or g/mol; (d) 60.05 amu or g/mol
2. (a) 123.896 amu or g/mol; (b) 18.015 amu or g/mol; (c) 164.086 amu or g/mol; (d) 60.052 amu or g/mol; (e) 342.297 amu or g/mol
3. (a) 56.107 amu or g/mol; (b) 54.091 amu or g/mol; (c) 199.9976 amu or g/mol; (d) 97.9950 amu or g/mol
4. Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.
5. Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.
6. The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.
7. (a) 256.528 g/mol; (b) 72.150 g mol^{-1}; (c) 378.103 g mol^{-1}; (d) 58.080 g mol^{-1}; (e) 180.158 g mol^{-1}
8. (a) 197.382 g mol^{-1}; (b) 257.163 g mol^{-1}; (c) 194.193 g mol^{-1}; (d) 60.056 g mol^{-1}; (e) 306.464 g mol^{-1}
9. (a) 0.819 g; (b) 307 g; (c) 0.23 g; (d) 1.235×10^6 g (1235 kg); (e) 765 g
10. (a) 99.41; (b) 2.27 g; (c) 3.5 g; (d) 222 kg; (e) 160.1 g
11. (a) 9.60 g; (b) 19.2 g; (c) 28.8 g
12. zirconium: 2.038×10^{23} atoms; 30.87 g; silicon: 2.038×10^{23} atoms; 9.504 g; oxygen: 8.151×10^{23} atoms; 21.66 g
13. $AlPO_4$: 1.000 mol Al_2Cl_6: 1.994 mol Al_2S_3: 3.00 mol
14. 3.113×10^{25} C atoms
15. 0.865 servings, or about 1 serving.
16. 20.0 g H_2O represents the least number of molecules since it has the least number of moles.
17. (a) % N = 82.24% % H = 17.76%; (b) % Na = 29.08% % S = 40.56% % O = 30.36%; (c) % Ca^{2+} = 38.76%
18. % NH_3 = 38.2%
19. (a) CS_2 (b) CH_2O
20. C_6H_6

21. $Mg_3Si_2H_3O_8$ (empirical formula), $Mg_6Si_4H_6O_{16}$ (molecular formula)
22. $C_{15}H_{15}N_3$

CHAPTER 8: CHEMICAL EQUATIONS

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- Components of a chemical equation
- Writing chemical compounds in a chemical reaction
- Balancing chemical reactions
- The 5 types of chemical reactions (combustion, combination, decomposition, single displacement and double displacement)

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- States of matter
- Elements
- Compounds
- Moles
- Molar Mass

Figure 8a Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. (credit: work courtesy of NASA/JPL-Caltech, JPL Image Policy.)

Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet (Figure 8a). The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

Attribution & References

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8.1 WRITING AND BALANCING CHEMICAL EQUATIONS

Learning Objectives

By the end of this section, you will be able to:

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular formats

The preceding chapter introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure 8.1a, with space-filling molecular models shown in the lower half of the figure.

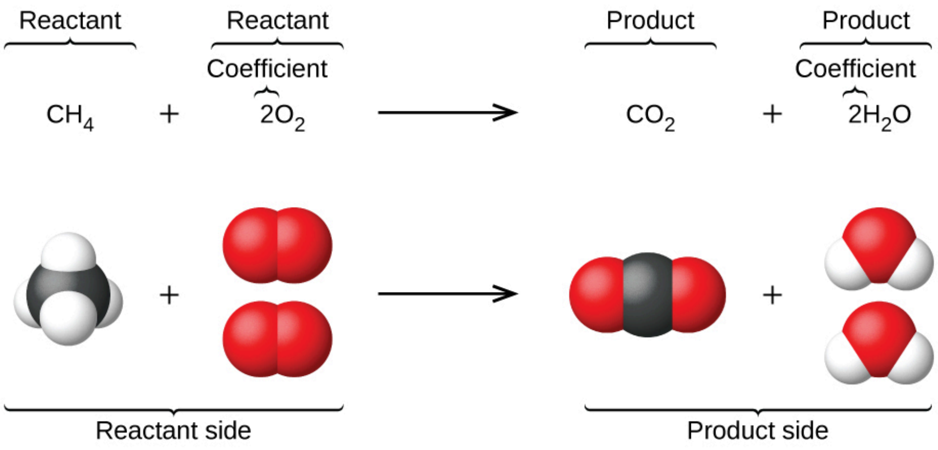

Figure 8.1a The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called products, and their formulas are placed on the right sight of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow (→) separates the reactant and **product** (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure 8.1b). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.
- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide

molecules and *2 moles* of water molecules.

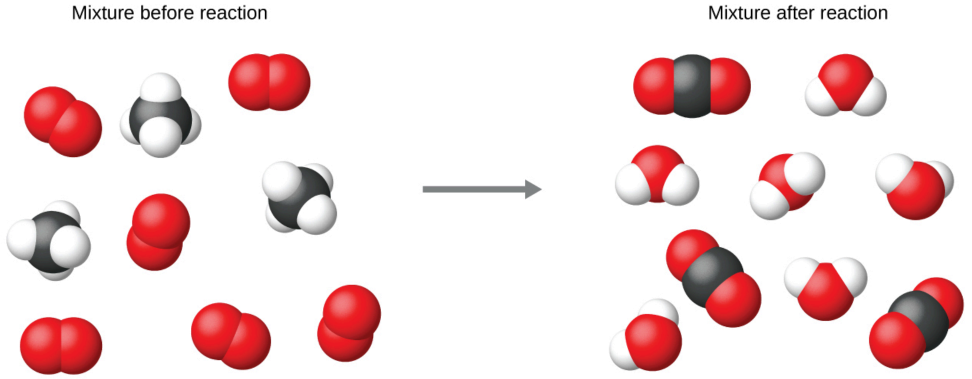

Figure 8.1b Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Balancing Equations

The chemical equations described above are **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the **reactant** and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$(1\ \text{CO}_2\ \text{molecule} \times \frac{2\ \text{O atoms}}{\text{CO}_2\ \text{molecule}}) + (2\ \text{H}_2\text{O molecule} \times \frac{1\ \text{O atom}}{\text{H}_2\text{O molecule}}) = 4\ \text{O atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

Tally Chart for Reaction of Methane and Oxygen to Yield Carbon Dioxide and Water

Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$H_2O \longrightarrow H_2 + O_2 \text{ (unbalanced)}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Tally Chart for Decomposition of Water to Yield Hydrogen and Oxygen #1

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2H_2O \longrightarrow H_2 + O_2 \text{ (unbalanced)}$$

Tally Chart for Decomposition of Water to Yield Hydrogen and Oxygen #2

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2H_2O \longrightarrow 2H_2 + O_2 \text{ (balanced)}$$

Tally Chart for Decomposition of Water to Yield Hydrogen and Oxygen #3

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 4	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$2H_2O \longrightarrow 2H_2 + O_2$$

Example 8.1a

Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \longrightarrow N_2O_5 \text{ (unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Tally Chart for Reaction of Nitrogen and Oxygen to Form Dinitrogen Pentoxide #1

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 2 = 2	1 × 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$N_2 + 5O_2 \longrightarrow 2N_2O_5 \text{ (unbalanced)}$$

Tally Chart for Reaction of Nitrogen and Oxygen to Form Dinitrogen Pentoxide #2

Element	Reactants	Products	Balanced?
N	1 ×× 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2N_2 + 5O_2 \longrightarrow 2N_2O_5$$

Tally Chart for Reaction of Nitrogen and Oxygen to Form Dinitrogen Pentoxide #3

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Exercise 8.1a

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Check Your Answer[1]

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$\mathrm{C_2H_6 + O_2 \longrightarrow H_2O + CO_2}\ \text{(unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$\mathrm{C_2H_6 + O_2 \longrightarrow 3H_2O + 2CO_2}\ \text{(unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

$$\mathrm{C_2H_6 + \frac{7}{2}O_2 \longrightarrow 3H_2O + 2CO_2}$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$\mathrm{2C_2H_6 + 7O_2 \longrightarrow 6H_2O + 4CO_2}$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$\mathrm{3N_2 + 9H_2 \longrightarrow 6NH_3}$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$\mathrm{N_2 + 3H_2 \longrightarrow 2NH_3}$$

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$\mathrm{2Na}(s) + \mathrm{2H_2O}(l) \longrightarrow \mathrm{2NaOH}(aq) + \mathrm{H_2}(g)$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

Endothermic vs. Exothermic Reactions

Sometimes ΔH for a chemical reaction is displayed which may be positive or negative. The number is assumed to be positive if it has no sign; a + sign can be added explicitly to avoid confusion. A chemical reaction that has a positive ΔH is said to be **endothermic** while a chemical reaction that has a negative ΔH is said to be **exothermic.**

What does it mean if the ΔH of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy change that accompanies the reaction can be shown in Figure 8.1c. It displays the energy of the reactants with some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in Figure 8.1d. If the ΔH of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

Source: "Endothermic vs. Exothermic Reactions" adapted by Adrienne Richards from Chapter 7: Enthalpy and Chemical Reactions In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY NC SA 4.0.

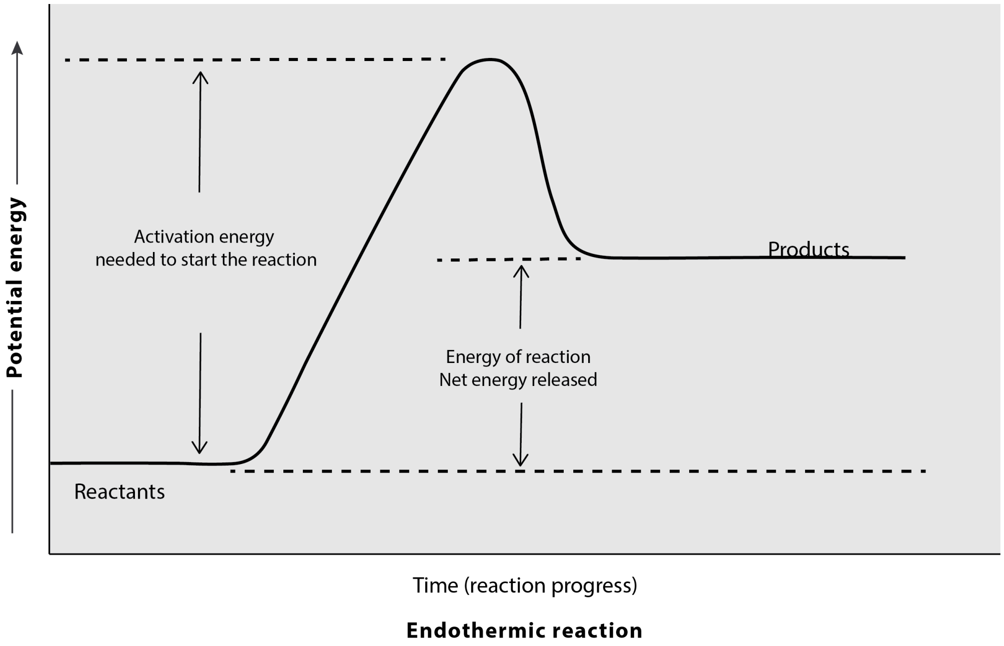

Figure 8.1c The diagram depicts the change in potential energies as the reaction progresses over time for endothermic reactions. (credit: graphics by Revathi Mahadevan, CC BY 4.0)

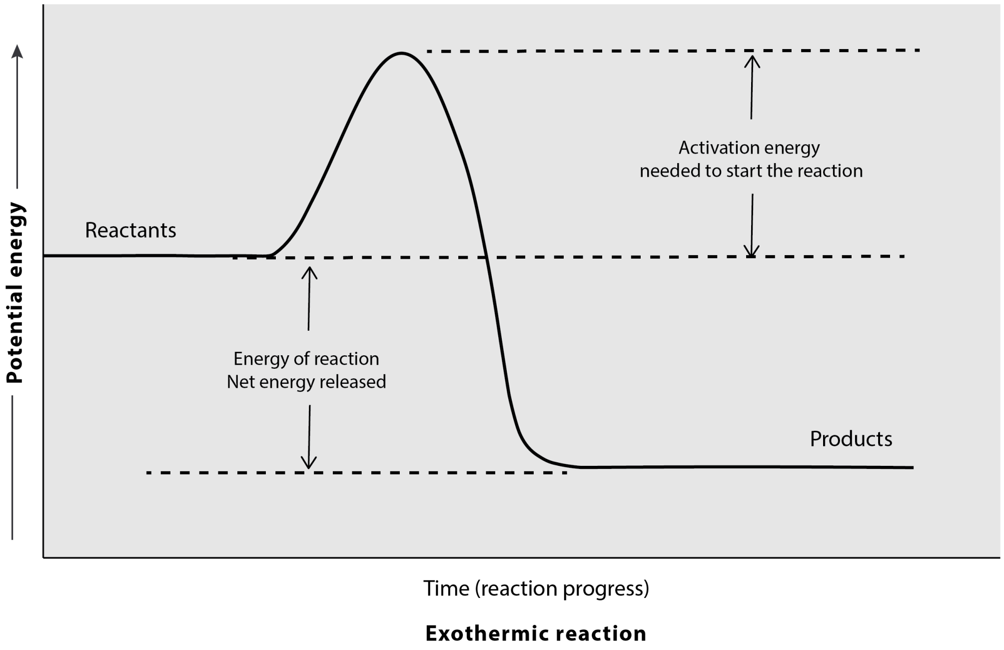

Figure 8.1d The diagram depicts the change in potential energies as the reaction progresses over time for exothermic reactions. (credit: graphics by Revathi Mahadevan, CC BY 4.0)

Exercise 8.1b

Practice using the following PhET simulation: Balancing Chemical Equations

Links to Interactive Learning Tools

Practice Balancing Chemical Equations from the Physics Classroom.

Practice Writing Balanced Equations from the Physics Classroom.

Practice Particles, Words and Formulas from the Physics Classroom.

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- Chapter 7: Enthalpy and Chemical Reactions In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA 4.0.

Notes

1. $2NH_4NO_3 \longrightarrow 2N_2 + O_2 + 4H_2O$

8.2 CLASSIFYING COMPOSITION, DECOMPOSITION, AND COMBUSTION REACTIONS

Learning Objectives

By the end of this section, you will be able to:

- Identify composition, decomposition, and combustion reactions.
- Predict the products of a combustion reaction.

Three classifications of chemical reactions will be reviewed in this section (composition, decomposition and combustion), while two additional chemical reactions (single and double displacement) will be explored in the proceeding section. Predicting the products in some of them may be difficult, but the reactions are still easy to recognize.

Watch Type of Chemical Reaction (5 mins)

A **composition reaction** (sometimes also called a *combination reaction* or a *synthesis reaction*) produces a single substance from multiple reactants. A single substance as a product is the key characteristic of the composition reaction. There may be a coefficient other than one for the substance, but if the reaction has only a single substance as a product, it can be called a composition reaction. In the reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$

water is produced from hydrogen and oxygen. Although there are two molecules of water being produced, there is only one substance—water—as a product. So this is a composition reaction.

A **decomposition reaction** starts from a single substance and produces more than one substance; that is, it decomposes. One substance as a reactant and more than one substance as the products is the key characteristic of a decomposition reaction. For example, if we look at the decomposition of sodium hydrogen carbonate (also known as sodium bicarbonate):

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(\ell)$$

We can see that sodium carbonate, carbon dioxide, and water are produced from the single substance sodium hydrogen carbonate.

Composition and decomposition reactions are difficult to predict; however, they should be easy to recognize.

Example 8.2a

Problems

Identify each equation as a composition reaction, a decomposition reaction, or neither.

1. $Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3$
2. $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$
3. $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + 4H_2O + N_2$

Solutions

1. In this equation, two substances combine to make a single substance. This is a composition reaction.
2. Two different substances react to make two new substances. This does not fit the definition of either a composition reaction or a decomposition reaction, so it is neither. In fact, you may recognize this as a double-replacement reaction.
3. A single substance reacts to make multiple substances. This is a decomposition reaction.

Exercise 8.2a

Identify the equation as a composition reaction, a decomposition reaction, or neither.

$$C_3H_8 \rightarrow C_3H_4 + 2H_2$$

Check Your Answer[1]

A **combustion reaction** occurs when a reactant combines with oxygen, many times from the atmosphere, to produce oxides of all other elements as products; any nitrogen in the reactant is converted to elemental nitrogen, N_2. Many reactants, called *fuels*, contain mostly carbon and hydrogen atoms, reacting with oxygen to produce CO_2 and H_2O. For example, the balanced chemical equation for the combustion of methane, CH_4, is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Kerosene can be approximated with the formula $C_{12}H_{26}$, and its combustion equation is

$$2C_{12}H_{26} + 37O_2 \rightarrow 24CO_2 + 26H_2O$$

Sometimes fuels contain oxygen atoms, which must be counted when balancing the chemical equation. One common fuel is ethanol, C_2H_5OH, whose combustion equation is

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

If nitrogen is present in the original fuel, it is converted to N_2, not to a nitrogen-oxygen compound. Thus, for the combustion of the fuel dinitroethylene, whose formula is $C_2H_2N_2O_4$, we have

$$2C_2H_2N_2O_4 + O_2 \rightarrow 4CO_2 + 2H_2O + 2N_2$$

Example 8.2b

Problems

Complete and balance each combustion equation.

1. the combustion of propane, C_3H_8
2. the combustion of ammonia, NH_3

Solutions

1. The products of the reaction are CO_2 and H_2O, so our unbalanced equation is $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$. Balancing (and you may have to go back and forth a few times to balance this), we get $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$.
2. The nitrogen atoms in ammonia will react to make N_2, while the hydrogen atoms will react with O_2 to make H_2O, thus $NH_3 + O_2 \rightarrow N_2 + H_2O$. To balance this equation without fractions (which is the convention), we get $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$.

Figure 8.2a Propane is a fuel used to provide heat for some homes. Propane is stored in large tanks like that shown here. (credit: work by vistavision, CC BY-NC-ND 2.0

Exercise 8.2b

Complete and balance the combustion equation for cyclopropanol, C_3H_6O.

Check Your Answer[2]

Attribution & References

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Notes

1. Decomposition
2. $C_3H_6O + 4O_2 \rightarrow 3CO_2 + 3H_2O$

8.3 CLASSIFYING AND COMPLETING SINGLE- AND DOUBLE-DISPLACEMENT REACTIONS

Learning Objectives

By the end of this section, you will be able to:

- Identify chemical reactions as single-replacement reactions and double-replacement reactions.
- Use the periodic table, an activity series, or solubility rules to predict whether single-replacement reactions or double-replacement reactions will occur.

Up to now, we have presented chemical reactions as a topic, but we have not discussed how the products of a chemical reaction can be predicted. Here we will begin our study of certain types of chemical reactions that allow us to predict what the products of the reaction will be.

A **single-replacement reaction** is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products. For example:

$$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$

is an example of a single-replacement reaction. The hydrogen atoms in HCl are replaced by Zn atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is:

$$2NaCl(aq) + F_2(g) \rightarrow 2NaF(s) + Cl_2(g)$$

Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single-replacement reaction is that there is one element as a reactant and another element as a product.

Not all proposed single-replacement reactions will occur between two given reactants. This is most easily demonstrated with fluorine, chlorine, bromine, and iodine. Collectively, these elements are called the *halogens* and are in the next-to-last column on the periodic table (see Figure 8.3a “Halogens on the Periodic Table”). The elements on top of the column will replace the elements below them on the periodic table but not the other way around. Thus, the reaction represented by:

$$CaI_2(s) + Cl_2(g) \rightarrow CaCl_2(s) + I_2(s)$$

This reaction will occur, but the reaction

$$CaF_2(s) + Br_2(\ell) \rightarrow CaBr_2(s) + F_2(g)$$

will not because bromine is below fluorine on the periodic table. This is just one of many ways the periodic table helps us understand chemistry.

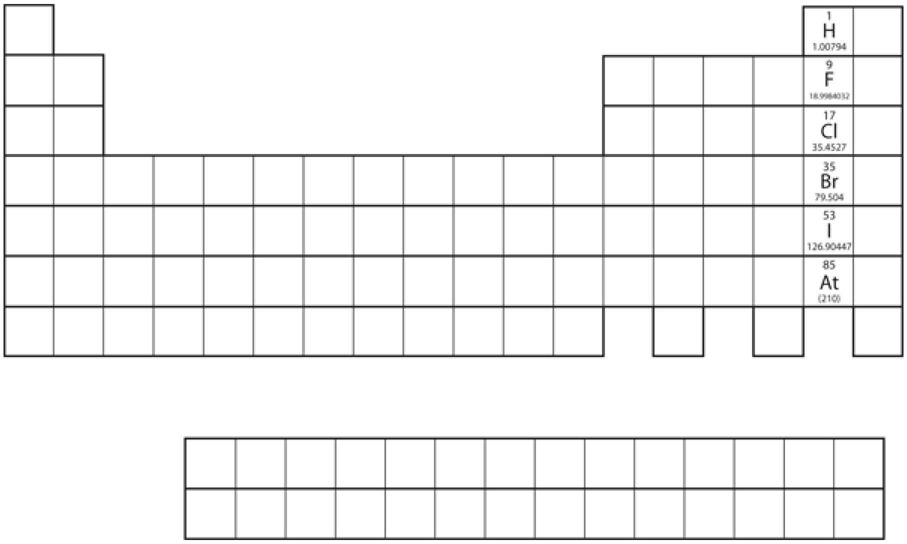

Figure 8.3a "Halogens on the Periodic Table." The halogens are the elements in the next-to-last column on the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Introductory Chemistry: 1st Canadian Edition*, CC BY-NC-SA 4.0).

Example 8.3a

Problems

Will a single-replacement reaction occur? If so, identify the products.

1. $MgCl_2 + I_2 \rightarrow ?$
2. $CaBr_2 + F_2 \rightarrow ?$

Solutions

1. Because iodine is below chlorine on the periodic table, a single-replacement reaction will not occur.
2. Because fluorine is above bromine on the periodic table, a single-replacement reaction will occur, and the products of the reaction will be CaF_2 and Br_2.

Exercise 8.3a

Will a single-replacement reaction occur? If so, identify the products.

$$FeI_2 + Cl_2 \rightarrow ?$$

Check Your Answer[1]

Chemical reactivity trends are easy to predict when replacing anions in simple ionic compounds—simply use their relative positions on the periodic table. However, when replacing the cations, the trends are not as straightforward. This is partly because there are so many elements that can form cations; an element in one column on the periodic table may replace another element nearby, or it may not. A list called the **activity series** does the same thing the periodic table does for halogens: it lists the elements that will replace elements below them in single-replacement reactions. A simple activity series is shown below.

Activity Series for Cation Replacement in Single-Replacement Reactions

1. Li
2. K
3. Ba
4. Sr
5. Ca
6. Na
7. Mg
8. Al
9. Mn
10. Zn
11. Cr
12. Fe
13. Ni
14. Sn
15. Pb
16. H_2
17. Cu
18. Hg
19. Ag
20. Pd
21. Pt
22. Au

An element with a lower number will replace an element with a higher number in compounds undergoing a single-replacement reaction. Elements will not replace elements with a lower number in compounds. In many sources, these elements are listed as a long vertical list (not numbered).

Using the activity series is similar to using the positions of the halogens on the periodic table. An element on top will replace an element below it in compounds undergoing a single-replacement reaction. Elements will not replace elements above them in compounds.

Example 8.3b

Problems

Use the activity series to predict the products, if any, of each equation.

1. $FeCl_2 + Zn \rightarrow ?$
2. $HNO_3 + Au \rightarrow ?$

Solutions

1. Because zinc is above iron in the activity series, it will replace iron in the compound. The products of this single-replacement reaction are $ZnCl_2$ and Fe.
2. Gold is below hydrogen in the activity series. As such, it will not replace hydrogen in a compound with the nitrate ion. No reaction is predicted.

Exercise 8.3b

Use the activity series to predict the products, if any, of this equation.

$$AlPO_4 + Mg \rightarrow ?$$

Check Your Answer[2]

A **double-replacement reaction** occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products.

Evidence of a double replacement reaction are the following:

1. The evolution of heat
2. The formation of an insoluble precipitate

3. The production of gas bubbles

Source: (Hein et al., 2013, p. 153)

An example of a double replacement reaction is:

$$CuCl_2(aq) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2AgCl(s)$$

There are two equivalent ways of considering a double-replacement equation: either the cations are swapped, or the anions are swapped. (You cannot swap both; you would end up with the same substances you started with.) Either perspective should allow you to predict the proper products, as long as you pair a cation with an anion and not a cation with a cation or an anion with an anion.

Example 8.3c

Problem

Predict the products of this double-replacement equation: $BaCl_2$ + Na_2SO_4 → ?

Solution

Thinking about the reaction as either switching the cations or switching the anions, we would expect the products to be $BaSO_4$ and NaCl.

Exercise 8.3c

Predict the products of this double-replacement equation: KBr + $AgNO_3$ → ?

Check Your Answer[3]

Predicting whether a double-replacement reaction occurs is somewhat more difficult than predicting a single-replacement reaction. However, there is one type of double-replacement reaction that we can predict: the precipitation reaction. A **precipitation reaction** occurs when two ionic compounds are dissolved in water and form a new ionic compound that does not dissolve; this new compound falls out of solution as a solid **precipitate**. The formation of a solid precipitate is the driving force that makes the reaction proceed.

For example, consider the double-replacement reaction between Na_2SO_4 and $SrCl_2$. The double-replacement reaction products are NaCl and $SrSO_4$. The balanced chemical equation is:

$$Na_2SO_4(aq) + SrCl_2(aq) \rightarrow 2NaCl(aq) + SrSO_4(s)$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution as noted by the (s) in the product formed within the chemical equation (Figure 8.3b "Double-Replacement Reactions").

Figure 8.3b "Double-Replacement Reactions." Some double-replacement reactions are obvious because you can see a solid precipitate coming out of the solution. (credit: work by Choij, PD)

General examples of double replacement reactions include:

- Neutralization of an Acid and a Base (heat is released by the production of water)

Example: \ce{HCl (aq) + NaOH (aq) → NaCl (aq) + H2O (l)}

- Metal Oxide + Acid (heat is released by the production of water)

Example: $\mathrm{CuO + 2\,HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + H_2O(l)}$

- Formation of an Insoluble Precipitate (precipitate is formed as indicated by the (s) in the product)

Example: $\mathrm{BaCl_2(aq) + 2\,AgNO_3(aq) \rightarrow 2\,AgCl(s) + Ba(NO_3)_2(aq)}$

- Formation of a Gas (a gas is formed as indicated by the (g) in the product).

Example: $$\mathrm{H_2SO_4(aq) + NaCl(s) \rightarrow NaHSO_4(s) + HCl(g)}$$

Source: (Hein et al., 2013, p. 153)

Example 8.3d

Problem

What are the products of the double-replacement reaction

1. $NaOH + FeCl_2 \rightarrow ?$

Solution

1. The balanced chemical equation is: $2NaOH(aq) + FeCl_2(aq) \rightarrow 2NaCl(aq) + Fe(OH)_2(s)$

Exercise 8.3d

Check Your Learning Exercise (Text Version)
For the following reactions, classify the reaction as one of the following: single displacement, decomposition, combination, double displacement, or combustion.

a. $2CH_3OH\ (g) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 4H_2O\ (g)$
b. $2H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g)$
c. $P_4\ (s) + 5O_2\ (g) \rightarrow P_4O_{10}\ (s)$
d. $2Al\ (s) + 3H_2SO_4\ (aq) \rightarrow Al_2(SO_4)_3\ (s) + 3H_2\ (g)$
e. $ZnS\ (s) + 2HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2S\ (g)$

Check Your Answer[4]

Source: “Exercise 8.3d” by Adrienne Richards is adapted from “7.2 Classifying Chemical

Reactions" from General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Indigenous Perspective: Natural Chemical Reactions

Figure 8.3c Birch tree (credit: work by Dallas Reedy, Unsplash license)

Chemical reactions related to Indigenous practices in Canada are used as a teaching tool, described within the document "Chemical Reactions: Background Information Science 10 [PDF]".

The teaching tool was developed in collaboration with the Steward Resources Center, the Government of Saskatchewan and the Saskatchewan Teachers' Federation.

Chemical reactions are involved in practices passed down from one generation to the next. This is important so that First Nations and Metis communities can make their own supplies by following the methods from previous generations. These practices include the process of making natural bleach, jellies, medicines, meals and household products.

Links to Interactive Learning Tools

Practice Chemical Reaction Types from the Physics Classroom.

Practice Writing Chemical Equations from the Physics Classroom.

Attribution & References

Except where otherwise noted, this page is adapted by Adrienne Richards from "Chapter 4: Chemical Reactions and Equations: Types of Chemical Reactions: Single and Double-Displacement Reactions"

In*Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA 4.0.

Reference

Hein, M., Pattison, S., Arena, S., & Best, L. (2013). *Introduction to general, organic, and biochemistry* (11th ed.). John Wiley & Sons, Inc.

Notes

1. Yes; $FeCl_2$ and I_2
2. $Mg_3(PO_4)_2$ and Al
3. KNO_3 and AgBr
4. (a) combustion; (b) decomposition; (c) combination; (d) single displacement; (e)double displacement

CHAPTER 8 - SUMMARY

8.1 Writing and Balancing Chemical Equations

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products.

8.2 Classifying Composition, Decomposition and Combustion Reactions

Three types of chemical reactions were learned: a composition reaction, a decomposition reaction and a combustion reaction. A composition reaction produces a single substance from multiple reactants. A decomposition reaction produces multiple products from a single reactant. Combustion reactions are the combination of some compound with oxygen to make oxides of the other elements as products (although nitrogen atoms react to make N_2).

8.3 Classifying and Completing Single- and Double-Displacement Reactions

Two types of chemical reactions were learned: single-replacement and double-replacement. A single-replacement reaction replaces one element for another in a compound. The periodic table or an activity series can help predict whether single-replacement reactions occur. A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds. A precipitation reaction is a double-replacement reaction in which one product is a solid precipitate.

Attribution & References

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- 8.2 and 8.3 – "Chapter 4: Chemical Reactions and Equations: Composition, Decomposition, and Combustion Reactions"and "Chapter 4: Types of Chemical Reactions: Single and Double Displacement Reactions" In*Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA 4.0.

CHAPTER 8 - REVIEW

8.1 Writing and Balancing Chemical Equations

1. What does it mean to say an equation is balanced? Why is it important for an equation to be balanced? **Check Answer:** [1]
2. Balance the following equations: **Check Answer:** [2]
   a. $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + \text{HCl}(aq)$
   b. $\text{Cu}(s) + \text{HNO}_3(aq) \longrightarrow \text{Cu(NO}_3)_2(aq) + \text{H}_2\text{O}(l) + \text{NO}(g)$
   c. $\text{H}_2(g) + \text{I}_2(s) \longrightarrow \text{HI}(s)$
   d. $\text{Fe}(s) + \text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$
   e. $\text{Na}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{NaOH}(aq) + \text{H}_2(g)$
   f. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + \text{H}_2\text{O}(g)$
   g. $\text{P}_4(s) + \text{Cl}_2(g) \longrightarrow \text{PCl}_3(l)$
   h. $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + \text{Cl}_2(g)$
3. Balance the following equations:
   a. $\text{Ag}(s) + \text{H}_2\text{S}(g) + \text{O}_2(g) \longrightarrow \text{Ag}_2\text{S}(s) + \text{H}_2\text{O}(l)$
   b. $\text{P}_4(s) + \text{O}_2(g) \longrightarrow \text{P}_4\text{O}_{10}(s)$
   c. $\text{Pb}(s) + \text{H}_2\text{O}(l) + \text{O}_2(g) \longrightarrow \text{Pb(OH)}_2(s)$
   d. $\text{Fe}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Fe}_3\text{O}_4(s) + \text{H}_2(g)$
   e. $\text{Sc}_2\text{O}_3(s) + \text{SO}_3(l) \longrightarrow \text{Sc}_2(\text{SO}_4)_3(s)$
   f. $\text{Ca}_3(\text{PO}_4)_2(aq) + \text{H}_3\text{PO}_4(aq) \longrightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2(aq)$
   g. $\text{Al}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{Al}_2(\text{SO}_4)_3(s) + \text{H}_2(g)$
   h. $\text{TiCl}_4(s) + \text{H}_2\text{O}(g) \longrightarrow \text{TiO}_2(s) + \text{HCl}(g)$
4. Write a balanced molecular equation describing each of the following chemical reactions. **Check Answer:** [3]
   a. Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.
   b. Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapour.
   c. Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.
   d. Water vapour reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.
5. Write a balanced equation describing each of the following chemical reactions.

  - a. Solid potassium chlorate, $KClO_3$, decomposes to form solid potassium chloride and diatomic oxygen gas.
  - b. Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6.
  - c. When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.
  - d. Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

6. Colourful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen. **Check Answer:** [4]
   - a. Write the formulas of barium nitrate and potassium chlorate.
   - b. The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.
   - c. The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.
   - d. Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

8.2 Classifying Composition, Decomposition and Combustion Reactions

1. Which is a composition reaction and which is not? **Check Answer:** [5]
   - a. $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$
   - b. $CaO + CO_2 \rightarrow CaCO_3$
2. Which is a composition reaction and which is not?
   - a. $H_2 + Cl_2 \rightarrow 2HCl$
   - b. $2HBr + Cl_2 \rightarrow 2HCl + Br_2$
3. Which is a composition reaction and which is not? **Check Answer:** [6]
   - a. $2SO_2 + O_2 \rightarrow 2SO_3$
   - b. $6C + 3H_2 \rightarrow C_6H_6$
4. Which is a composition reaction and which is not?
   - a. $4Na + 2C + 3O_2 \rightarrow 2Na_2CO_3$
   - b. $Na_2CO_3 \rightarrow Na_2O + CO_2$
5. Which is a decomposition reaction and which is not? **Check Answer:** [7]
   - a. $HCl + NaOH \rightarrow NaCl + H_2O$
   - b. $CaCO_3 \rightarrow CaO + CO_2$
6. Which is a decomposition reaction and which is not?

   a. $3O_2 \rightarrow 2O_3$
   b. $2KClO_3 \rightarrow 2KCl + 3O_2$
7. Which is a decomposition reaction and which is not? **Check Answer:** [8]
   a. $Na_2O + CO_2 \rightarrow Na_2CO_3$
   b. $H_2SO_3 \rightarrow H_2O + SO_2$
8. Which is a decomposition reaction and which is not?
   a. $2C_7H_5N_3O_6 \rightarrow 3N_2 + 5H_2O + 7CO + 7C$
   b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
9. Which is a combustion reaction and which is not? **Check Answer:** [9]
   a. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
   b. $2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$
10. Which is a combustion reaction and which is not?
    a. $CH_4 + 2F_2 \rightarrow CF_4 + 2H_2$
    b. $2H_2 + O_2 \rightarrow 2H_2O$
11. Which is a combustion reaction and which is not? **Check Answer:** [10]
    a. $P_4 + 5O_2 \rightarrow 2P_2O_5$
    b. $2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$
12. Which is a combustion reaction and which is not?
    a. $C_2H_4 + O_2 \rightarrow C_2H_4O_2$
    b. $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$
13. Is it possible for a composition reaction to also be a combustion reaction? Give an example to support your case. **Check Answer:** [11]
14. Is it possible for a decomposition reaction to also be a combustion reaction? Give an example to support your case.
15. Complete and balance each combustion equation. **Check Answer:** [12]
    a. $C_4H_9OH + O_2 \rightarrow ?$
    b. $CH_3NO_2 + O_2 \rightarrow ?$
16. Complete and balance each combustion equation.
    a. $B_2H_6 + O_2 \rightarrow ?$ (The oxide of boron formed is B_2O_3.)
    b. $Al_2S_3 + O_2 \rightarrow ?$ (The oxide of sulfur formed is SO_2.)
    c. $Al_2S_3 + O_2 \rightarrow ?$ (The oxide of sulfur formed is SO_3.)

8.3 Classifying and Completing Single- and Double-Displacement Reactions

1. What are the general characteristics that help you recognize single-replacement reactions? **Check Answer:** [13]

2. What are the general characteristics that help you recognize double-replacement reactions?
3. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation. **Check Answer:** [14]
    a. $Zn + Fe(NO_3)_2 \rightarrow ?$
    b. $F_2 + FeI_3 \rightarrow ?$
4. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Li + MgSO_4 \rightarrow ?$
    b. $NaBr + Cl_2 \rightarrow ?$
5. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation. **Check Answer:** [15]
    a. $Sn + H_2SO_4 \rightarrow ?$
    b. $Al + NiBr_2 \rightarrow ?$
6. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Mg + HCl \rightarrow ?$
    b. $HI + Br_2 \rightarrow ?$
7. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation. **Check Answer:** [16]
    a. $FeCl_2 + Br_2 \rightarrow ?$
    b. $Fe(NO_3)_3 + Al \rightarrow ?$
8. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $Zn + Fe_3(PO_4)_2 \rightarrow ?$
    b. $Ag + HNO_3 \rightarrow ?$
9. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation. **Check Answer:** [17]
    a. $NaI + Cl_2 \rightarrow ?$
    b. $AgCl + Au \rightarrow ?$
10. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $Pt + H_3PO_4 \rightarrow ?$
    b. $Li + H_2O \rightarrow ?$ (Hint: treat H_2O as if it were composed of H^+ and OH^- ions.)
11. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation. **Check Answer:** [18]
    a. $Zn(NO_3)_2 + NaOH \rightarrow ?$
    b. $HCl + Na_2S \rightarrow ?$

12. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Ca(C_2H_3O_2)_2 + HNO_3 \rightarrow ?$
    b. $Na_2CO_3 + Sr(NO_2)_2 \rightarrow ?$
13. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation. **Check Answer:** [19]
    a. $Pb(NO_3)_2 + KBr \rightarrow ?$
    b. $K_2O + MgCO_3 \rightarrow ?$
14. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Sn(OH)_2 + FeBr_3 \rightarrow ?$
    b. $CsNO_3 + KCl \rightarrow ?$
15. Assuming that the double-replacement reaction occurs, predict the product and write a balanced chemical equation. **Check Answer:** [20]
    a. $Pb(NO_3)_2 + KBr \rightarrow ?$
16. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation. **Check Answer:** [21]
    a. $K_3PO_4 + SrCl_2 \rightarrow ?$
    b. $NaOH + MgCl_2 \rightarrow ?$

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- "Exercises 4.1. Writing and Balancing Chemical Equations" in *Chemistry 2e (OpenStax)* by Paul Flowers, Klaus Theopold, Richard Langley, & William R. Robinson, licensed under CC BY 4.0. Access for free at Chemistry 2e (OpenStax). Questions 1-7.
- "Chapter 4: Chemical Reactions and Equations: Composition, Decomposition, and Combustion Reactions"and "Chapter 4: Types of Chemical Reactions: Single and Double Displacement Reactions" In*Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA 4.0. Questions 8-38.

Notes

1. An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

2. (a) $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + 2\text{HCl}(aq)$; (b) $3\text{Cu}(s) + 8\text{HNO}_3(aq) \longrightarrow 3\text{Cu(NO}_3)_2(aq) + 4\text{H}_2\text{O}(l) + 2\text{NO}(g)$; (c) $\text{H}_2(g) + \text{I}_2(s) \longrightarrow 2\text{HI}(s)$; (d) $4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$; (e) $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$; (f) $(\text{NH}_4)_2\text{Cr}_2 2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + 4\text{H}_2\text{O}(l)$; (g) $\text{P}_4(s) + 6\text{Cl}_2(g) \longrightarrow 4\text{PCl}_3(l)$; (h) $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + 2\text{Cl}_2(g)$;
3. (a) $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$; (b) $2\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \longrightarrow 8\text{CO}_2(g) + 10\text{H}_2\text{O}(g)$; (c) $\text{MgCl}_2(aq) + 2\text{NaOH}(aq) \longrightarrow \text{Mg(OH)}_2(s) + 2\text{NaCl}(aq)$; (d) $2\text{H}_2\text{O}(g) + 2\text{Na}(s) \longrightarrow 2\text{NaOH}(s) + \text{H}_2(g)$;
4. (a) $\text{Ba(NO}_3)_2$, KClO_3; (b) $2\text{KClO}_3(s) \longrightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$; (c) $2\text{Ba(NO}_3)_2(s) \longrightarrow 2\text{BaO}(s) + 2\text{N}_2(g) + 5\text{O}_2(g)$; (d) $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s)$; $4\text{Al}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Al}_2\text{O}_3(g)$; $4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$;
5. a. not composition; b. composition
6. a. composition; b. composition
7. a. not decomposition; b. decomposition
8. a. not decomposition; b. decomposition
9. a. combustion; b. combustion
10. a. combustion; b. combustion
11. Yes; $2H_2 + O_2 \rightarrow 2H_2O$ (answers will vary)
12. a. $C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$ b. $4CH_3NO_2 + 3O_2 \rightarrow 4CO_2 + 6H_2O + 2N_2$
13. One element replaces another element in a compound.
14. a. $Zn + Fe(NO_3)_2 \rightarrow Zn(NO_3)_2 + Fe$ b. $3F_2 + 2FeI_3 \rightarrow 3I_2 + 2FeF_3$
15. a. $Sn + H_2SO_4 \rightarrow SnSO_4 + H_2$ b. $2Al + 3NiBr_2 \rightarrow 2AlBr_3 + 3Ni$
16. a. No reaction occurs. b. . $Fe(NO_3)_3 + Al \rightarrow Al(NO_3)_3 + Fe$
17. a. $2NaI + Cl_2 \rightarrow 2NaCl + I_2$ b. No reaction occurs.
18. a. $Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$ b. $2HCl + Na_2S \rightarrow 2NaCl + H_2S$
19. a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2 + 2KNO_3$ b. $K_2O + MgCO_3 \rightarrow K_2CO_3 + MgO$
20. . a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2(s) + 2KNO_3$
21. a. $2K_3PO_4 + 3SrCl_2 \rightarrow Sr_3(PO_4)_2(s) + 6KCl$ b. $2NaOH + MgCl_2 \rightarrow 2NaCl + Mg(OH)_2(s)$

CHAPTER 9: STOICHIOMETRY USING CHEMICAL EQUATIONS

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- Quantitative components within a chemical reaction
- Mole ratios within a chemical reaction
- Stoichiometry analysis of a chemical reaction involving moles and mass
- Determine the limiting reactant and the excess reactant in a chemical reaction

- Determine the percent yield within a chemical reaction

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Nomenclature
- Compounds
- Mole quantities and calculations
- Molar mass

Figure 9a Example of a chemistry building that required stoichiometric quantifications to be constructed. (credit: Photo by Bree Evans, Unsplash license)

At Contrived State University in Anytown, Ohio, a new building was dedicated in March 2010 to house the College of Education. The 100,000-square-foot building has enough office space to accommodate 86 full-time faculty members and 167 full-time staff.

In a fit of monetary excess, the university administration offered to buy new furniture (desks and chairs) and computer workstations for all faculty and staff members moving into the new building. However, to save on long-term energy and materials costs, the university offered to buy only 1 laser printer per 10 employees, with the plan to network the printers together.

How many laser printers did the administration have to buy? It is rather simple to show that 26 laser printers are needed for all the employees. However, what if a chemist was calculating quantities for a chemical reaction? Interestingly enough, similar calculations can be performed for chemicals as well as laser printers.

In filling a new office building with furniture and equipment, managers do calculations similar to those performed by scientists doing chemical reactions.

We have already established that quantities are important in science, especially in chemistry. It is important to make accurate measurements of a variety of quantities when performing experiments. However, it is also important to be able to relate one measured quantity to another, unmeasured quantity. In this chapter, we will consider how we manipulate quantities to relate them to each other.

Attribution & References

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9.1 STOICHIOMETRY BASICS

Learning Objectives

By the end of this section, you will be able to:

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's **stoichiometry**, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Food preparation, for example, offers an appropriate comparison. A recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix} + \frac{3}{4} \text{ cup milk} + 1 \text{ egg} \longrightarrow 8 \text{ pancakes}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \cancel{\text{pancakes}} \times \frac{1 \text{ egg}}{8 \cancel{\text{pancakes}}} = 3 \text{ eggs}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\ \text{NH}_3\ \text{molecules}}{3\ \text{H}_2\ \text{molecules}}\ \text{or}\ \frac{2\ \text{doz NH}_3\ \text{molecules}}{3\ \text{doz H}_2\ \text{molecules}}\ \text{or}\ \frac{2\ \text{mol NH}_3\ \text{molecules}}{3\ \text{mol H}_2\ \text{molecules}}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Watch **Determining the Mole Ratio (6 mins)**

Example 9.1a

Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure 9.1a)?

$$2\text{Al} + 3\text{I}_2 \longrightarrow 2\text{AlI}_3$$

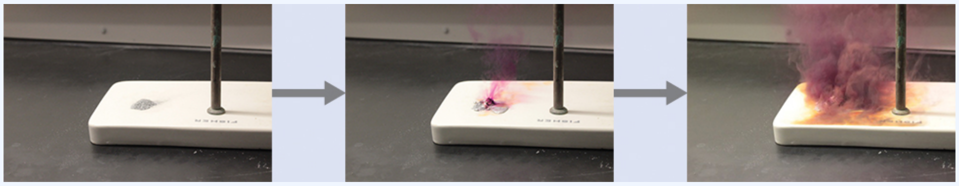
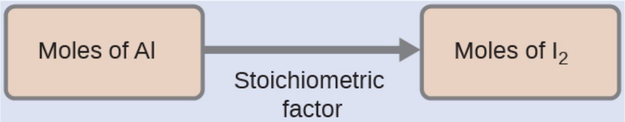


Figure 9.1a Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapour. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ \text{mol}\ \text{I}_2}{2\ \text{mol Al}}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$0.429\ \cancel{\text{mol Al}} \times \frac{3\ \text{mol}\ \text{I}_2}{2\ \cancel{\text{mol Al}}}$$

$$= 0.644\ \text{mol}\ \text{I}_2$$

Exercise 9.1a

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation:

$$3\text{Ca(OH)}_2 + 2\text{H}_3\text{PO}_4 \longrightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O}?$$

Check Your Answer[1]

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related.

Exercise 9.1b

Practice using the following PhET simulation: Reactants, Products, and Leftovers

Link to Interactive Learning Tools

Practice Mole-to-mole ratios from eCampusOntario H5P Studio.

Practice Stoichiometry – Relationships (Apprentice Difficulty Level ONLY) from The Physics Classroom.

Attribution & References

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Notes

1. 2.04 mol $Ca(OH)_2$

9.2 MOLE-MASS AND MASS-MASS CALCULATIONS

Learning Objectives

By the end of this section, you will be able to:

- From a given number of moles of a substance, calculate the mass of another substance involved using the balanced chemical equation.
- From a given mass of a substance, calculate the moles of another substance involved using the balanced chemical equation.
- From a given mass of a substance, calculate the mass of another substance involved using the balanced chemical equation.

Mole-mole calculations are not the only type of calculations that can be performed using balanced chemical equations. Recall that the molar mass can be determined from a chemical formula and used as a conversion factor. We can add that conversion factor as another step in a calculation to make a **mole-mass calculation**, where we start with a given number of moles of a substance and calculate the mass of another substance involved in the chemical equation, or vice versa.

For example, suppose we have the balanced chemical equation:

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

Suppose we know we have 123.2 g of Cl_2. How can we determine how many moles of $AlCl_3$ we will get when the reaction is complete? First and foremost, *chemical equations are not balanced in terms of grams; they are balanced in terms of moles*. So to use the balanced chemical equation to relate an amount of Cl_2 to an amount of $AlCl_3$, we need to convert the given amount of Cl_2 into moles. We know how to do this by simply using the molar mass of Cl_2 as a conversion factor. The molar mass of Cl_2 (which we get from the atomic mass of Cl from the periodic table) is 70.90 g/mol. We must invert this fraction so that the units cancel properly:

$$123.2\ \cancel{\text{g Cl}_2} \times \frac{1\ \text{mol Cl}_2}{70.90\ \cancel{\text{g Cl}_2}} = 1.738\ \text{mol Cl}_2$$

Now that we have the quantity in moles, we can use the balanced chemical equation to construct a conversion factor that relates the number of moles of Cl_2 to the number of moles of $AlCl_3$. The numbers in the conversion factor come from the coefficients in the balanced chemical equation:

$$\frac{2\ \text{mol AlCl}_3}{3\ \text{mol Cl}_2}$$

Using this conversion factor with the molar quantity we calculated above, we get:

$$1.738\ \cancel{\text{mol Cl}_2} \times \frac{2\ \text{mol AlCl}_3}{3\ \cancel{\text{mol Cl}_2}} = 1.159\ \text{mol AlCl}_3$$

So, we will get 1.159 mol of $AlCl_3$ if we react 123.2 g of Cl_2.

In this last example, we did the calculation in two steps. However, it is mathematically equivalent to perform the two calculations sequentially on one line:

$$123.2\ \cancel{\text{g Cl}_2} \times \frac{1\ \cancel{\text{mol Cl}_2}}{70.90\ \cancel{\text{g Cl}_2}} \times \frac{2\ \text{mol AlCl}_3}{3\ \cancel{\text{mol Cl}_2}} = 1.159\ \text{mol AlCl}_3$$

The units still cancel appropriately, and we get the same numerical answer in the end. Sometimes the answer may be slightly different from doing it one step at a time because of rounding of the intermediate answers, but the final answers should be effectively the same.

Example 9.2a

Problem

How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Solution

We will do this in two steps: convert the mass of $AlCl_3$ to moles and then use the balanced chemical equation to find the number of moles of HCl formed. The molar mass of $AlCl_3$ is 133.33 g/mol, which we have to invert to get the appropriate conversion factor:

$$1.87\ \cancel{\text{mol AlCl}_3} \times \frac{6\ \text{mol HCl}}{2\ \cancel{\text{mol AlCl}_3}} = 5.61\ \text{mol HCl}$$

Now we can use this quantity to determine the number of moles of HCl that will form. From the balanced chemical equation, we construct a conversion factor between the number of moles of $AlCl_3$ and the number of moles of HCl:

$$\frac{6\ \text{mol HCl}}{2\ \text{mol AlCl}_3}$$

Applying this conversion factor to the quantity of $AlCl_3$, we get:

$$1.87\ \cancel{\text{mol AlCl}_3} \times \frac{6\ \text{mol HCl}}{2\ \cancel{\text{mol AlCl}_3}} = 5.61\ \text{mol HCl}$$

Alternatively, we could have done this in one line:

$$249\ \cancel{\text{g AlCl}_3} \times \frac{1\ \cancel{\text{mol AlCl}_3}}{133.33\ \cancel{\text{g AlCl}_3}} \times \frac{6\ \text{mol HCl}}{2\ \cancel{\text{mol AlCl}_3}} = 5.60\ \text{mol HCl}$$

The last digit in our final answer is slightly different because of rounding differences, but the answer is essentially the same.

Exercise 9.2a

How many moles of Al_2O_3 will be produced when 23.9 g of H_2O are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Check Your Answer[1]

A variation of the mole-mass calculation is to start with an amount in moles and then determine an amount of another substance in grams. The steps are the same but are performed in reverse order.

Example 9.2b

Problem

How many grams of NH_3 will be produced when 33.9 mol of H_2 are reacted according to this chemical equation?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Solution

The conversions are the same, but they are applied in a different order. Start by using the balanced chemical equation to convert to moles of another substance and then use its molar mass to determine the mass of the final substance. In two steps, we have:

$$33.9\ \cancel{\text{mol H}_2} \times \frac{2\ \text{mol NH}_3}{3\ \cancel{\text{mol H}_2}} = 22.6\ \text{mol NH}_3$$

Now, using the molar mass of NH_3, which is 17.03 g/mol, we get:

$$22.6\ \cancel{\text{mol NH}_3} \times \frac{17.03\ \text{g NH}_3}{1\ \cancel{\text{mol NH}_3}} = 385\ \text{g NH}_3$$

Exercise 9.2b

How many grams of N_2 are needed to produce 2.17 mol of NH_3 when reacted according to this chemical equation?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Check Your Answer[2]

It should be a trivial task now to extend the calculations to **mass-mass calculations**, in which we start with a mass of some substance and end with the mass of another substance in the chemical reaction. For this type of calculation, the molar masses of two different substances must be used—be sure to keep track of which is which. Again, however, it is important to emphasize that before the balanced chemical reaction is used, the mass quantity must first be converted to moles. Then the coefficients of the balanced chemical reaction can be used to convert to moles of another substance, which can then be converted to a mass.

For example, let us determine the number of grams of SO_3 that can be produced by the reaction of 45.3 g of SO_2 and O_2:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

First, we convert the given amount, 45.3 g of SO_2, to moles of SO_2 using its molar mass (64.06 g/mol):

$$45.3\ \cancel{\text{g SO}_2} \times \frac{1\ \text{mol SO}_2}{64.06\ \cancel{\text{g SO}_2}} = 0.707\ \text{mol SO}_2$$

Second, we use the balanced chemical reaction to convert from moles of SO_2 to moles of SO_3:

$$0.707\ \cancel{\text{mol SO}_2} \times \frac{2\ \text{mol SO}_3}{2\ \cancel{\text{mol SO}_2}} = 0.707\ \text{mol SO}_3$$

Finally, we use the molar mass of SO_3 (80.06 g/mol) to convert to the mass of SO_3:

$$0.707\ \cancel{\text{mol SO}_3} \times \frac{80.06\ \text{g SO}_3}{1\ \cancel{\text{mol SO}_3}} = 56.6\ \text{g SO}_3$$

We can also perform all three steps sequentially, writing them on one line as:

$$45.3\ \cancel{\text{g SO}_2} \times \frac{1\ \cancel{\text{mol SO}_2}}{64.06\ \cancel{\text{g SO}_2}} \times \frac{2\ \cancel{\text{mol SO}_3}}{2\ \cancel{\text{mol SO}_2}} \times \frac{80.06\ \text{g SO}_3}{1\ \cancel{\text{mol SO}_3}} = 56.6\ \text{g SO}_3$$

We get the same answer. Note how the initial and all the intermediate units cancel, leaving grams of SO_3, which is what we are looking for, as our final answer.

Example 9.2c

Problem

What mass of Mg will be produced when 86.4 g of K are reacted?

$$MgCl_2(s) + 2K(s) \rightarrow Mg(s) + 2KCl(s)$$

Solution

We will simply follow the steps:

mass K → mol K → mol Mg → mass Mg

In addition to the balanced chemical equation, we need the molar masses of K (39.09 g/mol) and Mg (24.31 g/mol). In one line,

$$86.4\ \cancel{\text{g K}} \times \frac{1\ \cancel{\text{mol K}}}{39.09\ \cancel{\text{g K}}} \times \frac{1\ \cancel{\text{mol Mg}}}{2\ \cancel{\text{mol K}}} \times \frac{24.31\ \text{g Mg}}{1\ \cancel{\text{mol Mg}}} = 26.87\ \text{Mg}$$

Exercise 9.2c

What mass of H_2 will be produced when 122 g of Zn are reacted?

$$\text{Zn(s)} + 2\ \text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$$

Check Your Answer[3]

Example 9.2d

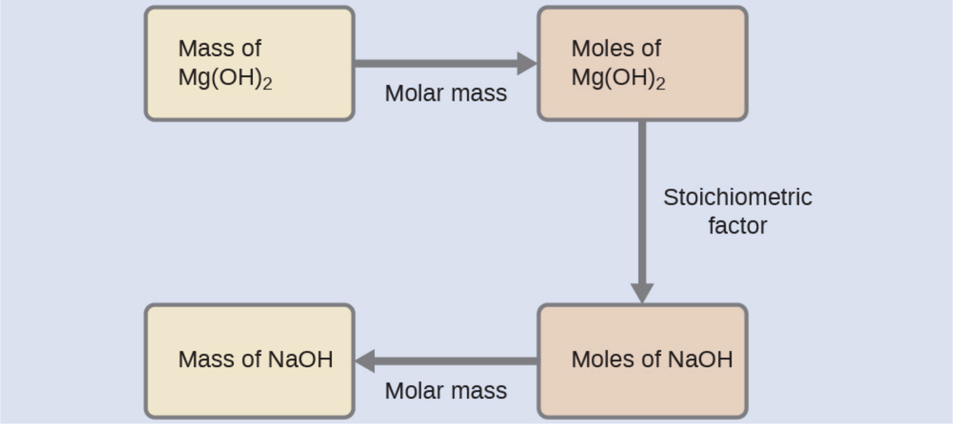
Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$\text{MgCl}_2(aq) + 2\text{NaOH}(aq) \longrightarrow \text{Mg(OH)}_2(s) + \text{NaCl}(aq)$$

Solution

The approach used previously in Example 1 and Example 2 is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16\ \cancel{\text{g Mg(OH)}_2} \times \frac{1\ \cancel{\text{mol Mg(OH)}_2}}{58.3\ \cancel{\text{g Mg(OH)}_2}} \times \frac{2\ \cancel{\text{mol NaOH}}}{1\ \cancel{\text{mol Mg(OH)}_2}} \times \frac{40.0\ \text{g NaOH}}{1\ \cancel{\text{mol NaOH}}} = 22\ \text{g NaOH}$$

Exercise 9.2d

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is:

$$4\text{Ga} + 3\text{O}_2 \longrightarrow 2\text{Ga}_2\text{O}_3$$

Check Your Answer[4]

Example 9.2e

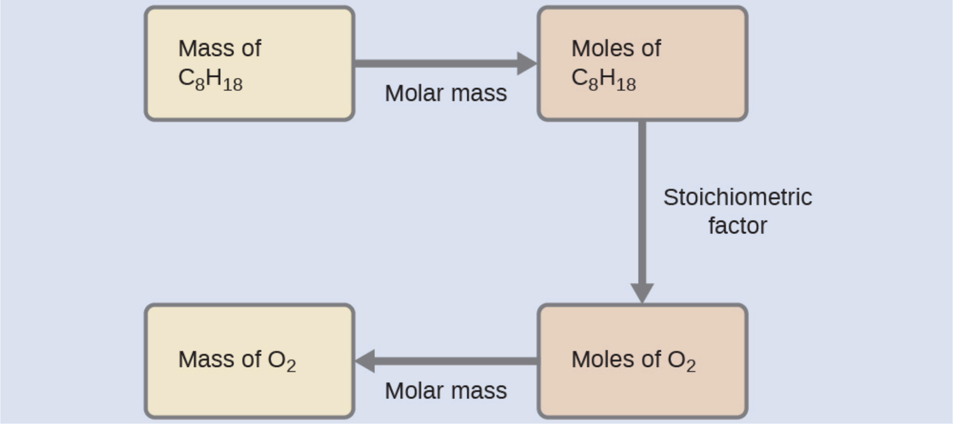
Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\text{C}_8\text{H}_{18} + 25\text{O}_2 \longrightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}$$

Solution

The approach required here is the same as for the Example 3, differing only in that the provided and requested masses are both for reactant species.



$$702\,\cancel{\text{g C}_8\text{H}_{18}} \times \frac{1\,\cancel{\text{mol C}_8\text{H}_{18}}}{114.23\,\cancel{\text{g C}_8\text{H}_{18}}} \times \frac{25\,\cancel{\text{mol O}_2}}{2\,\cancel{\text{mol C}_8\text{H}_{18}}} \times \frac{32.00\text{ g O}_2}{\cancel{\text{mol O}_2}} = 2.46 \times 10^3\text{ g O}_2$$

Exercise 9.2e

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation:

$$\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$$

Check Your Answer[5]

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure 9.2a provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

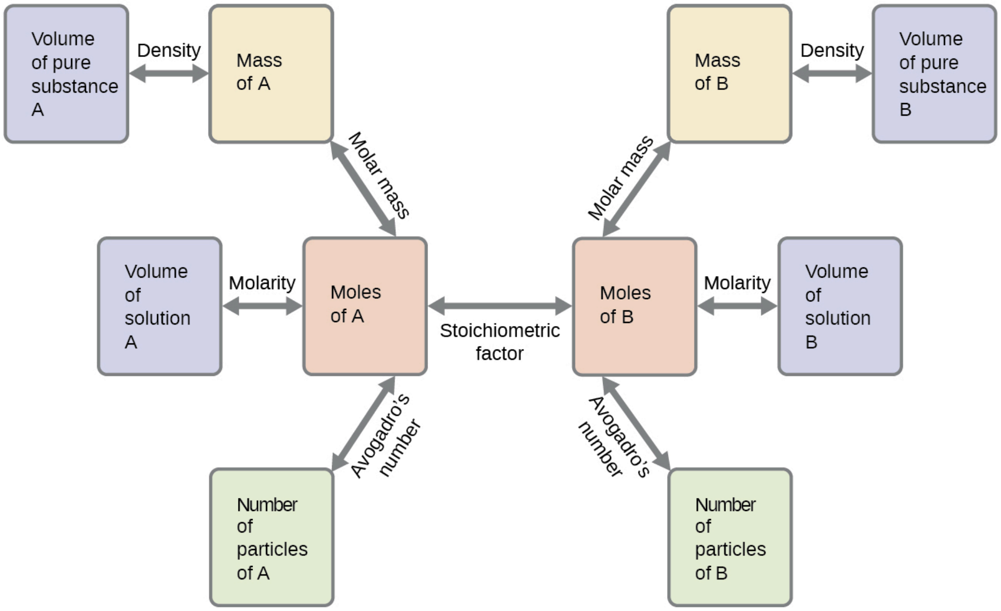


Figure 9.2a The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Airbags

Airbags (Figure 9.2b) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\mathrm{NaN_3}(s) \longrightarrow 3\mathrm{N_2}(g) + 2\mathrm{Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.

Figure 9.2b Airbags deploy upon impact to minimize serious injuries to passengers. (credit: work by Jon Seidman, CC BY 2.0)

Links to Interactive Learning Tools

Practice Stoichiometry – Relationships (all levels) from The Physics Classroom.

Attribution & References

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- "Chapter 5: Stoichiometry and The Mole: Mole-Mass and Mass-Mass Calculations" In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA

4.0.

Notes

1. 0.442 mol
2. 30.4 g (Note: here we go from a product to a reactant, showing that mole-mass problems can begin and end with any substance in the chemical equation.)
3. 3.77 g
4. 39.0 g Ga_2O_3
5. 13

9.3 LIMITING REACTANTS

Learning Objectives

By the end of this section, you will be able to:

- Explain the concepts of limiting reactants/reagents.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 9.2a):

$$1 \text{ slice of cheese} + 2 \text{ slices of bread} \longrightarrow 1 \text{ sandwich}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

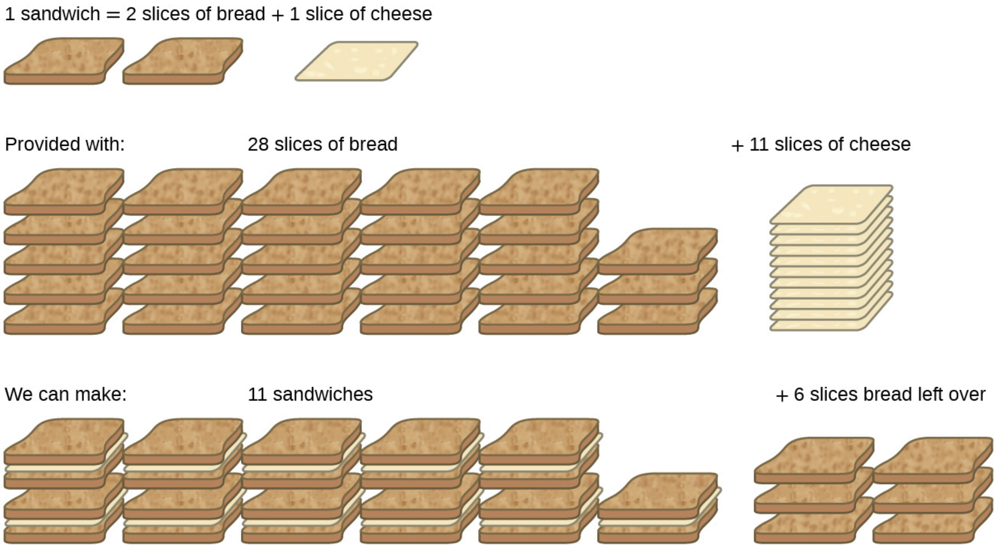

Figure 9.3a Sandwich making can illustrate the concepts of limiting and excess reactants (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$H_2(s) + Cl_2(g) \longrightarrow 2HCl(g)$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the **limiting reactant**, and the other substance is the **excess reactant**. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example in the previous paragraph, complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 3\text{ mol }H_2 \times \frac{2\text{ mol HCl}}{1\text{ mol }H_2} = 6\text{ mol HCl}$$

Complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 2\ \text{mol Cl}_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol Cl}_2} = 4\ \text{mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure 9.2b).

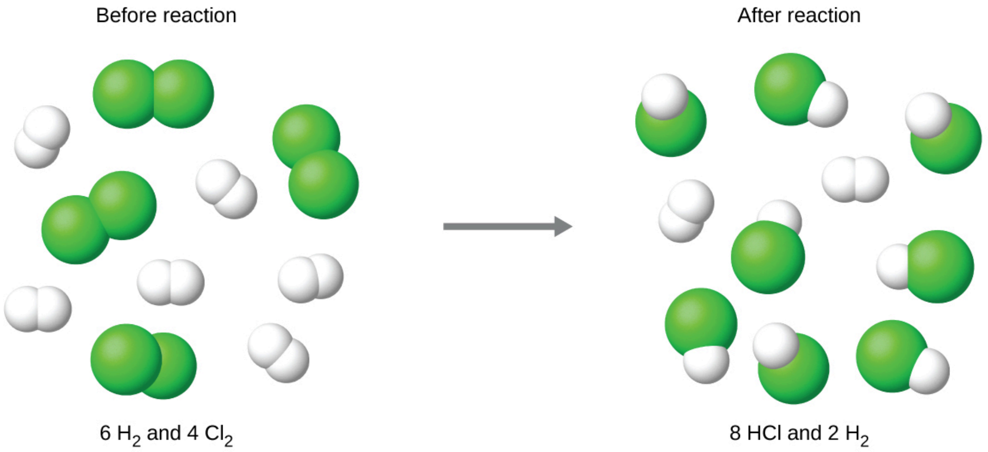

Figure 9.3b When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 9.3a

Practice using the following PhET simulation: Reactants, Products, and Leftovers

Example 9.3a

Identifying the Limiting Reactant and Calculate Max Amount of Product Produced

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\text{Si}(s) + 2\text{N}_2(g) \longrightarrow \text{Si}_3\text{N}_4(s)$$

A) Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

B) How many grams of silicon nitride are produced?

Solution

A) Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$\text{mol Si} = 2.00\ \cancel{\text{g Si}} \times \frac{1\text{ mol Si}}{28.09\ \cancel{\text{g Si}}} = 0.0712\text{ mol Si}$$

$$\text{mol N}_2 = 1.50\ \cancel{\text{g N}_2} \times \frac{1\text{ mol N}_2}{28.09\ \cancel{\text{g N}_2}} = 0.0535\text{ mol N}_2$$

The provided Si:N_2 molar ratio is:

$$\frac{0.0712\text{ mol Si}}{0.0535\text{ mol N}_2} = \frac{1.33\text{ mol Si}}{1\text{mol N}_2}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3\text{ mol Si}}{2\text{ mol N}_2} = \frac{1.5\text{ mol Si}}{1\text{ mol N}_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

$$\text{mol Si}_3\text{N}_4\text{ produced} = 0.0712\text{ mol Si} \times \frac{1\text{ mol Si}_3\text{N}_4}{3\text{ mol Si}} = \\ 0.0237\text{ mol Si}_3\text{N}_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol Si}_3\text{N}_4\text{ produced} = 0.0535\text{ mol N}_2 \times \frac{1\text{ mol Si}_3\text{N}_4}{2\text{ mol N}_2} = \\ 0.0268\text{ mol Si}_3\text{N}_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

B) In order to determine the maximum amount of product produced, first the limiting reactant has to be determined. In part A, the limiting reactant was determined to be silicon. Therefore, the moles of silicon nitride produced by silicon will be used to calculate how many grams of silicon nitride is produced.

$$0.0237 \text{ mol } \mathrm{Si_3N_4} \times \frac{140.28 \text{ g } \mathrm{Si_3N_4}}{1 \text{ mol } \mathrm{Si_3N_4}} = 3.32 \text{ grams } \mathrm{Si_3N_4}$$

Exercise 9.3b

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water? How many grams of water is produced?

Check Your Answer[1]

Indigenous Perspective: Science of Bannock

Bannock is a staple food in many Indigenous communities throughout Canada. Here is an Anishinaabeg example of the science of Bannock.

Watch The Science of Bannock (23 mins)

Attribution & References

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Notes

1. O_2 is limiting reactant, 22.5 g H_2O produced

9.4 REACTION YIELDS

Learning Objectives

By the end of this section, you will be able to:

- Explain the concepts of theoretical yield.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the **theoretical yield** of the reaction. In practice, the amount of product obtained is called the **actual yield**, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this chapter). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its **percent yield**:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

Example 9.4a

Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$\mathrm{CuSO_4}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

$$1.274\ \cancel{\mathrm{g\ CuSO_4}} \times \frac{1\ \cancel{\mathrm{mol\ CuSO_4}}}{159.62\ \cancel{\mathrm{g\ CuSO_4}}} \times \frac{1\ \cancel{\mathrm{mol\ Cu}}}{1\cancel{\mathrm{mol\ CuSO_4}}} \times \frac{63.55\ \mathrm{g\ Cu}}{1\ \cancel{\mathrm{mol\ Cu}}} = 0.5072\ \mathrm{g\ Cu}$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

$$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$

$$\text{percent yield} = \left(\frac{0.392\ \mathrm{g\ Cu}}{0.5072\ \mathrm{g\ Cu}}\right) \times 100$$

$$= 77.3\%$$

Exercise 9.4a

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$\mathrm{CCl_4} + 2\mathrm{HF} \longrightarrow \mathrm{CF_2Cl_2} + 2\mathrm{HCl}$$

Check Your Answer[1]

Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry". One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure 9.4a). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.

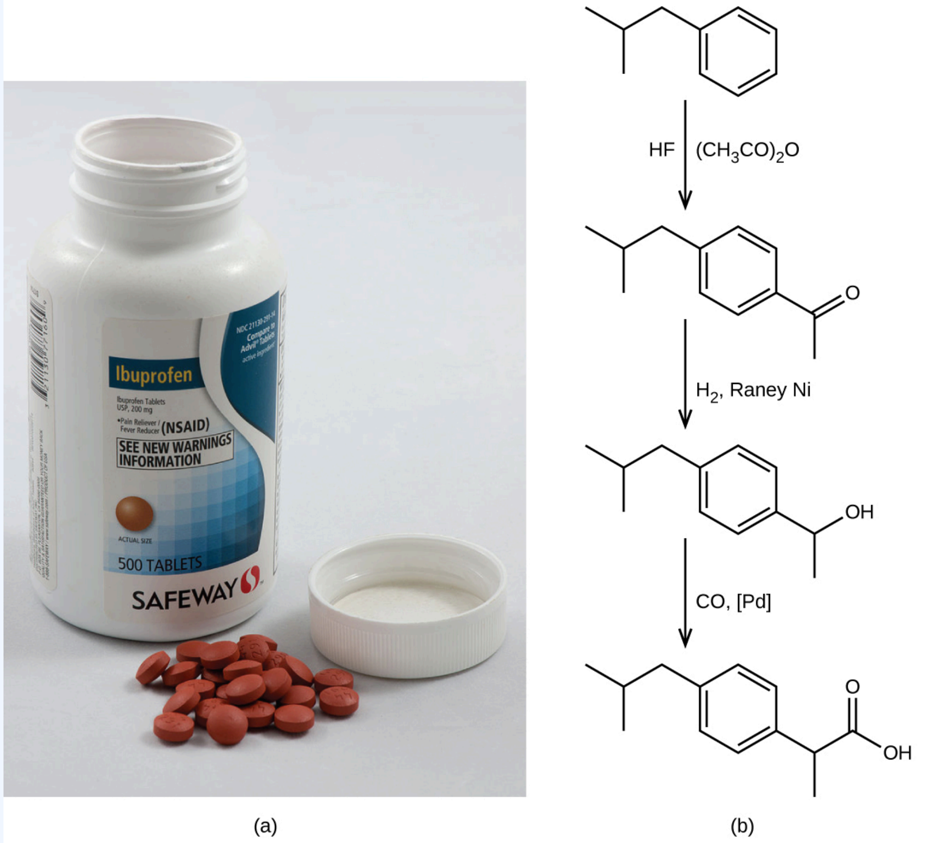

Figure 9.4a (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Chiara Coetzee, CC0)

Key Equations

- $\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$

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Notes

1. 48.3%

CHAPTER 9 - SUMMARY

9.1 Stoichiometric Basics

A balanced chemical equation may be used to describe a reaction’s stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties. Mole quantities of one substance can be related to mass quantities using a balanced chemical equation.

9.2 Mole-Mass and Mass-Mass Calculations

Mole quantities of one substance can be related to mass quantities using a balanced chemical equation. Mass quantities of one substance can be related to mass quantities using a balanced chemical equation. In all cases, quantities of a substance must be converted to moles before the balanced chemical equation can be used to convert to moles of another substance.

9.3 Limiting Reactants

When reactions are carried out using less-than-stoichiometric quantities of reactants, the amount of product generated will be determined by the limiting reactant.

9.4 Reaction Yields

The amount of product generated by a chemical reaction is its actual yield. This yield is often less than the amount of product predicted by the stoichiometry of the balanced chemical equation representing the reaction (its theoretical yield). The extent to which a reaction generates the theoretical amount of product is expressed as its percent yield.

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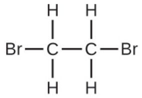
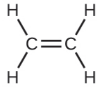
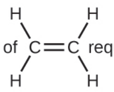
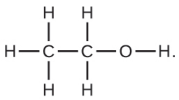
- "Chapter 5: Stoichiometry and The Mole: Mole-Mass and Mass-Mass Calculations" In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA 4.0. / Key takeaways section reused.

CHAPTER 9 - REVIEW

9.1 Stoichiometry Basics; and 9.2 Mole-Mass and Mass-Mass Calculations

1. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:
    a. The number of moles and the mass of chlorine, Cl_2, required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.
    b. The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.
    c. The number of moles and the mass of sodium nitrate, $NaNO_3$, required to produce 128 g of oxygen. ($NaNO_2$ is the other product.)
    d. The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.
    e. The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)
    f. The number of moles and the mass of  formed by the reaction of 12.85 g of  with an excess of Br_2.
2. Determine the number of moles and the mass requested for each reaction in Q.1 a) to f) above. **Check Answer:** [1]
3. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following
    a. The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce $MgCl_2$ and H_2.
    b. The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver(I) oxide.
    c. The number of moles and the mass of magnesium carbonate, $MgCO_3$, required to produce 283 g of carbon dioxide. (MgO is the other product.)
    d. The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene, C_2H_2, in an excess of oxygen.
    e. The number of moles and the mass of barium peroxide, BaO_2, needed to produce 2.500 kg of barium oxide, BaO (O_2 is the other product.)

f. The number of moles and the mass of  required to react with H_2O to produce 9.55 g of 

4. Determine the number of moles and the mass requested for each reaction in Q3. a) to f) above. **Check Answer:** [2]
5. I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation:

   $2CuCl_2 + 4KI \longrightarrow 2CuI + 4KCl + I_2.$

   (a) What mass of I_2 is produced?
6. Silver is often extracted from ores such as $K[Ag(CN)_2]$ and then recovered by the reaction $2K[Ag(CN)_2](aq) + Zn(s) \longrightarrow 2Ag(s) + Zn(CN)_2(aq) + 2KCN(aq)$(a) What mass of $Zn(CN)_2$ is produced? **Check Answer:** [3]
7. What mass of CO_2 is produced by the combustion of 1.00 mol of CH_4? **Check Answer:** [4]

   $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
8. What mass of H_2O is produced by the combustion of 1.00 mol of CH_4?

   $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
9. What mass of HgO is required to produce 0.692 mol of O_2? **Check Answer:** [5]

   $$2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$$
10. What mass of $NaHCO_3$ is needed to produce 2.659 mol of CO_2?

    $$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\ell) + CO_2(g)$$
11. How many moles of Al can be produced from 10.87 g of Ag? **Check Answer:** [6]

    $$Al(NO_3)_3(s) + 3Ag \rightarrow Al + 3AgNO_3$$
12. How many moles of HCl can be produced from 0.226 g of $SOCl_2$?

    $$SOCl_2(\ell) + H_2O(\ell) \rightarrow SO_2(g) + 2HCl(g)$$
13. How many moles of O_2 are needed to prepare 1.00 g of $Ca(NO_3)_2$? **Check Answer:** [7]

    $$Ca(s) + N_2(g) + 3O_2(g) \rightarrow Ca(NO_3)_2(s)$$
14. How many moles of C_2H_5OH are needed to generate 106.7 g of H_2O?

    $$C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$$
15. What mass of O_2 can be generated by the decomposition of 100.0 g of $NaClO_3$? **Check Answer:** [8]

    $$2NaClO_3 \rightarrow 2NaCl(s) + 3O_2(g)$$
16. What mass of Li_2O is needed to react with 1,060 g of CO_2?

$$Li_2O(aq) + CO_2(g) \rightarrow Li_2CO_3(aq)$$

17. What mass of Fe_2O_3 must be reacted to generate 324 g of Al_2O_3? **Check Answer:** [9]

$$Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

18. What mass of Fe is generated when 100.0 g of Al are reacted?

$$Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

19. What mass of MnO_2 is produced when 445 g of H_2O are reacted? **Check Answer:** [10]

$$H_2O(\ell) + 2MnO_4^-(aq) + Br^-(aq) \rightarrow BrO_3^-(aq) + 2MnO_2(s) + 2OH^-(aq)$$

20. What mass of $PbSO_4$ is produced when 29.6 g of H_2SO_4 are reacted?

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(\ell)$$

21. If 83.9 g of ZnO are formed, what mass of Mn_2O_3 is formed with it? **Check Answer:** [11]

$$Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$$

22. If 14.7 g of NO_2 are reacted, what mass of H_2O is reacted with it?

$$3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$$

23. If 88.4 g of CH_2S are reacted, what mass of HF is produced? **Check Answer:** [12]

$$CH_2S + 6F_2 \rightarrow CF_4 + 2HF + SF_6$$

24. If 100.0 g of Cl_2 are needed, what mass of NaOCl must be reacted?

$$NaOCl + HCl \rightarrow NaOH + Cl_2$$

25. What mass of silver oxide, Ag_2O, is required to produce 25.0 g of silver sulfadiazine, $AgC_{10}H_9N_4SO_2$, from the reaction of silver oxide and sulfadiazine?

$$2C_{10}H_{10}N_4SO_2 + Ag_2O \longrightarrow 2AgC_{10}H_9N_4SO_2 + H_2O$$

26. Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO_2, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much SiO_2 is required to produce 3.00 kg of SiC. **Check Answer:** [13]

9.3 Limiting Reactants and 9.4 Reaction Yields

1. Urea, $CO(NH_2)_2$, is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the CO_2 produced by combustion of 1.00×10^3kg of carbon followed by the reaction? **Check Answer:** [14]

$$CO_2(g) + 2NH_3(g) \longrightarrow CO(NH_2)_2(s) + H_2O(l)$$

2. In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?
3. A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbon by mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 litres per gallon).
4. What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine? **Check Answer:** [15]
5. Which of the postulates of Dalton's atomic theory explains why we can calculate a theoretical yield for a chemical reaction?
6. A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield? **Check Answer:** [16]
7. A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?
   $$\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(s)$$
8. Freon-12, CCl_2F_2, is prepared from CCl_4 by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of CCl_2F_2 from 32.9 g of CCl_4. Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield. **Check Answer:** [17]
9. Citric acid, $C_6H_8O_7$, a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. The equation representing this reaction is
   $$\mathrm{C_{12}H_{22}O_{11}} \ + \ \mathrm{H_2O} \ + 3\mathrm{O_2} \longrightarrow 2\mathrm{C_6H_8O_7} \ + \ 4\mathrm{H_2O}$$
   What mass of citric acid is produced from exactly 1 metric ton (1.000×10^3 kg) of sucrose if the yield is 92.30%?
10. Toluene, $C_6H_5CH_3$, is oxidized by air under carefully controlled conditions to benzoic acid, $C_6H_5CO_2H$, which is used to prepare the food preservative sodium benzoate, $C_6H_5CO_2Na$. What is the percent yield of a reaction that converts 1.000 kg of toluene to 1.21 kg of benzoic acid? **Check Answer:** [18]
    $$2\mathrm{C_6H_5CH_3} \ + \ 3\mathrm{O_2} \longrightarrow 2\mathrm{C_6H_5CO_2H} \ + \ 2\mathrm{H_2O}$$
11. In a laboratory experiment, the reaction of 3.0 mol of H_2 with 2.0 mol of I_2 produced 1.0 mol of HI. Determine the theoretical yield in grams and the percent yield for this reaction.
12. Outline the steps needed to determine the limiting reactant when 30.0 g of propane, C_3H_8, is burned with 75.0 g of oxygen. Determine the limiting reactant.
13. Outline the steps needed to determine the limiting reactant when 0.50 mol of Cr and 0.75 mol of H_3PO_4 react according to the following chemical equation.
    $$2\mathrm{Cr} \ + \ 2\mathrm{H_3PO_4} \longrightarrow 2\mathrm{CrPO_4} \ + \ 3\mathrm{H_2}$$

Determine the limiting reactant. **Check Answer:** [19]

14. What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation?
15. Uranium can be isolated from its ores by dissolving it as $UO_2(NO_3)_2$, then separating it as solid $UO_2(C_2O_4)·3H_2O$. Addition of 0.4031 g of sodium oxalate, $Na_2C_2O_4$, to a solution containing 1.481 g of uranyl nitrate, $UO_2(NO_3)_2$, yields 1.073 g of solid $UO_2(C_2O_4)·3H_2O$.
    $Na_2C_2O_4 + UO_2(NO_3)_2 + 3H_2O \longrightarrow UO_2(C_2O_4)·3H_2O + 2NaNO_3$
    Determine the limiting reactant and the percent yield of this reaction. **Check Answer:** [20]
16. The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.
    a. What is the limiting reactant when 0.200 mol of P_4 and 0.200 mol of O_2 react according to
    $$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
    b. Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

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- "Chapter 5: Stoichiometry and The Mole: Mole-Mass and Mass-Mass Calculations" In *Introductory Chemistry: 1st Canadian Edition* by David W. Ball and Jessica A. Key, licensed under CC BY-NC-SA 4.0. / Adapted exercises 7-24 for this page.

Notes

1. (a) 0.435 mol Na, 0.217 mol Cl_2, 15.4 g Cl_2; (b) 0.005780 mol HgO, 2.890×10^{-3} mol O_2, 9.248×10^{-2} g O_2; (c) 8.00 mol $NaNO_3$, 6.8×10^{2} g $NaNO_3$; (d) 1665 mol CO_2, 73.3 kg CO_2; (e) 18.86 mol CuO, 2.330 kg $CuCO_3$; (f) 0.4580 mol $C_2H_4Br_2$, 86.05 g $C_2H_4Br_2$
2. (a) 0.0686 mol Mg, 1.67 g Mg; (b) 2.701×10^{-3} mol O_2, 0.08644 g O_2; (c) 6.43 mol $MgCO_3$, 542 g $MgCO_3$ (d) 713 mol H_2O, 12.8 kg H_2O; (e) 16.31 mol BaO_2, 2762 g BaO_2; (f) 0.207 mol C_2H_4, 5.81 g C_2H_4
3. (a) 10.41 g $Zn(CN)_2$
4. 44.0 g
5. 3.00×10^{2} g
6. 0.0336 mol
7. 0.0183 mol

8. 45.1 g
9. 507 g
10. 4.30 × 10^3 g
11. 163 g
12. 76.7 g
13. $\mathrm{SiO_2 + 3C \longrightarrow SiC + 2CO}$, 4.50 kg SiO_2
14. 5.00 × 10^3 kg
15. The limiting reactant is Cl_2.
16. Percent yield = 31%
17. g CCl_4 → mol CCl_4 → mol CCl_2F_2 → g CCl_2F_2, percent yield = 48.3%
18. percent yield = 91.3%
19. The conversion needed is mol Cr→ mol H_3PO_4. Then compare the amount of Cr to the amount of acid present. Cr is the limiting reactant.
20. $Na_2C_2O_4$ is the limiting reactant. percent yield = 86.6%

CHAPTER 10: MODERN ATOMIC THEORY

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The nature of electromagnetic energy/radiation
- The Bohr model of the atom, how atoms emit light, and how the emission spectrum of

hydrogen supports the quantized nature of energy
- Wave nature of matter and the development of the quantum mechanical model
- Energy levels of electrons, shapes of orbitals, and development of the wave mechanical model
- The atomic structure of the first 18 elements and how principal energy levels fill with electrons in atoms beyond hydrogen. You will write electron configurations according to an element's electron filling order.
- Electron structures/configurations of atoms with atomic numbers greater than 18.
- Understand and predict general trends in atomic properties in the periodic table

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Rutherford's nuclear model of the atom including its subatomic particles of an atom
- Structure of the hydrogen atom
- Use the periodic table to identify the number of electrons in neutral atoms for various elements
- Identify group/family names and numbers on the periodic table
- Review common trends in periodic table including physical and chemical properties of metals and non metals and ion formation

Figure 10a The Crab Nebula consists of remnants of a supernova (the explosion of a star). NASA's Hubble Space Telescope produced this composite image. Measurements of the emitted light wavelengths enabled astronomers to identify the elements in the nebula, determining that it contains specific ions including S^+ (green filaments) and O^{2+} (red filaments). (credit: Crab Nebula by NASA, ESA, J. Hester and A. Loll (Arizona State University), PD).

In 1054, Chinese astronomers recorded the appearance of a "guest star" in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula (Figure 10.0a) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the coloured filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.

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References

Hester, J., & Loll, A. (2017, August). *The Crab Nebula*. NASA.

10.1 ELECTROMAGNETIC RADIATION

Learning Objectives

By the end of this section, you will be able to:

- Define the electromagnetic spectrum, and describe it in terms of wavelengths, frequencies, and energy
- Describe both the wave and particle nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Describe and explain the differences and similarities of each section of the electromagnetic spectrum and the applications of radiation from those sections

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a “corpuscular” view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton’s laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called “luminiferous aether” that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** (EMR) and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton’s laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell’s equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behaviour.

Watch the TED-Ed video Light waves, visible and invisible by Lucianne Walkowicz (5:56)

Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighbouring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ, the lowercase Greek letter lambda), a **frequency** (denoted by ν, the lowercase Greek letter nu), and an **amplitude**. As can be seen in Figure 10.1a, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometres (10^3 m) to picometres (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz (Hz)**, so 1 Hz = 1 s^{-1}. Common multiples of this unit are megahertz, (1 MHz = 1×10^6 Hz) and gigahertz (1 GHz = 1×10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure 10.1a, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

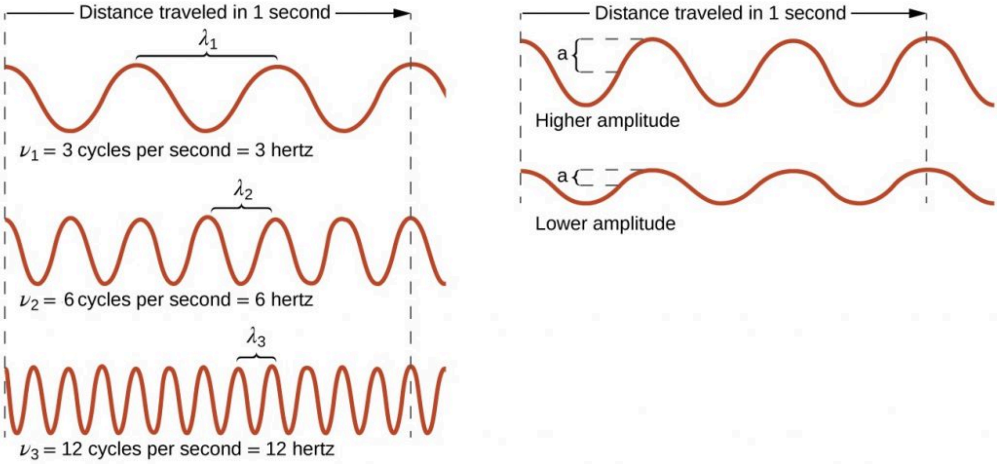


Figure 10.1a Comparing Wavelength, Frequency, and Speed using Sinusoidal Waves: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough (credit: *Chemistry (Open Stax)*, CC BY 4.0).

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8 \mathrm{ms}^{-1} = \lambda\nu$$

In summary, the properties of a wave are determined by:

- wave speed; all electromagnetic waves move through space at the same, constant speed of 2.99 x 10^8 ms^{-1}, which is the speed of light, c.
- height (amplitude)
- wavelength
- frequency

Electromagnetic radiation is also referred to as electromagnetic energy, which is a term used to describe the various energies that travel as wavelengths through space at the speed of light. Various types of electromagnetic radiation carry different amounts of energy. Wavelength is inversely proportional to its energy and frequency.

- Shorter wavelengths have higher frequency and have greater energy
- Longer wavelengths have lower frequency and less energy

This inverse proportionality is illustrated in Figure 10.1b – The Visible Light Spectrum of Electromagnetic Radiation. Each component colour in the visible spectrum of light has different wavelengths, with corresponding frequencies and energy. The spectrum ranges from dark red at 700 nm to violet at 400 nm. Longer wavelengths have lower frequency and carry less energy; shorter wavelengths have higher frequency and carry more energy.

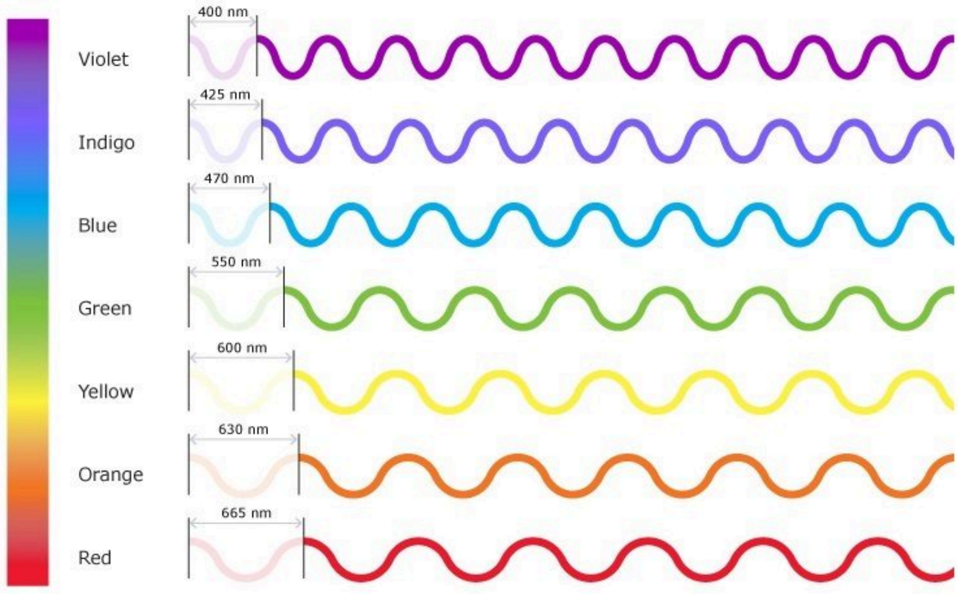


Figure 10.1b The Visible Light Spectrum of Electromagnetic Radiation: The Visual Spectrum of Electromagnetic Radiation: The visible spectrum is illustrated showing the wavelengths of each of the component colours. The spectrum ranges from dark red at 700 nm to violet at 400 nm. Longer wavelengths have lower frequency and carry less energy; Shorter wavelengths have higher frequency and carry more energy. (credit: Colours of Light by Science Learning Hub – Pokapū Akoranga Pūtaiao, University of Waikato, Educational Use.)

The inverse proportionality for a broader range of all types of electromagnetic energy is illustrated in Figure 10.1c. Each of the various colours of visible light has specific frequencies (energy amounts) and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

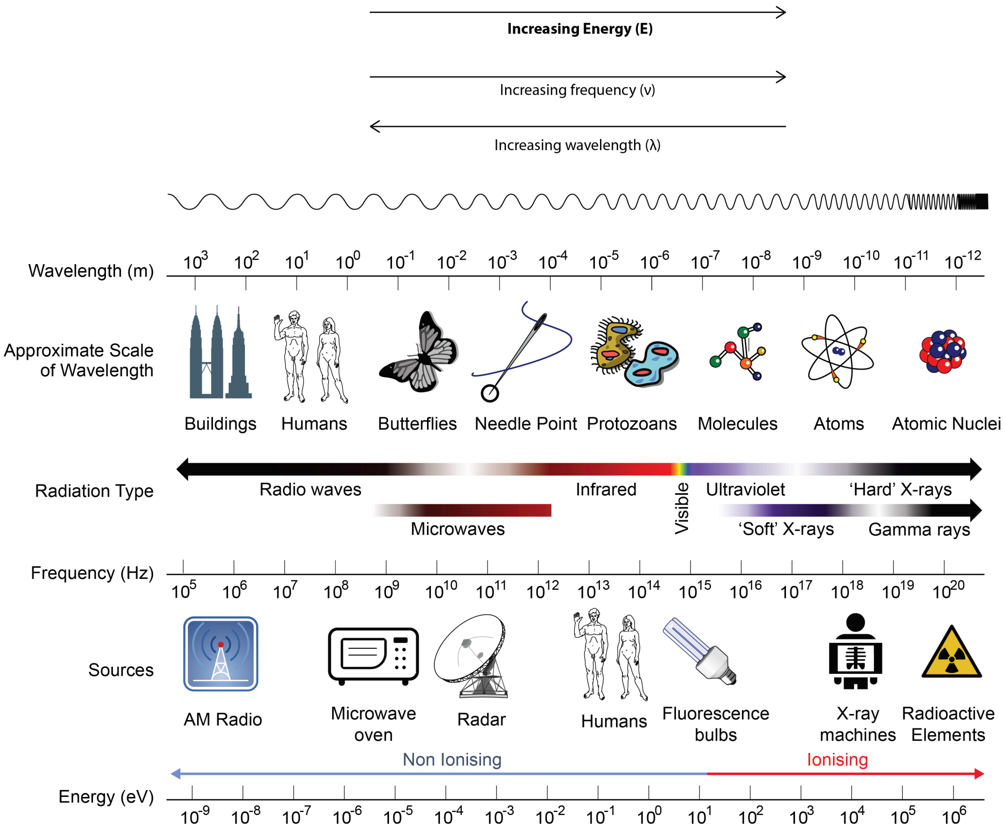


Figure 10.1c The Electromagnetic Spectrum: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit: modification of work by Dinksbumf, Inductiveload, NASA, CC BY-SA 3.0. / Adapted by Revathi Mahadevan to include energy, frequency & wavelength trends).

Example 10.1a

For the following example, reference Figure 10.1b – The Visible Light Spectrum of Electromagnetic Radiation.

Compare green light (550nm) and red light (665nm) from the visual light portion of the electromagnetic spectrum and answer the following questions:

1. Which colour of light, red or green, has a shorter wavelength?
2. Which colour of light, red or green, has a lower frequency?
3. Which colour of light, red or green, contains lower energy?

Solution

1. Green light has a shorter wavelength than red light
2. Red light has lower frequency since it has a longer wavelength than green light
3. Red light contains less energy since it has a lower frequency compared to green light

Exercise 10.1a

For the following exercises, reference Figure 10.1b – The Visible Light Spectrum of Electromagnetic Radiation.

Check Your Learning Exercise (Text Version)
Instructions: Answer the following questions related to Wavelength, Frequency, and Energy of Electromagnetic Radiation

1. True or False? Wavelength is inversely proportional to its energy and frequency
2. True or False? Longer wavelengths have lower frequency and less energy
3. True or False? Shorter wavelengths have higher frequency and have greater the energy
4. Review the word list provided which contains seven words or terms. Choose a word or phase to fill in the (BLANK) to make the statements correct. Each word will be used once. WORD LIST: frequency (v), wavelength (λ), electromagnetic spectrum, greater, less, shorter, longer
    a. [BLANK] wavelengths have higher frequency and [BLANK] energy
    b. [BLANK] is the distance between two peaks or troughs in a wave of given amplitude(height).
    c. [BLANK] is the number of waves (cycles) per second that pass a given point in space.
    d. [BLANK] wavelengths have lower frequency and [BLANK] energy.
    e. Visible light accounts for a very small portion of the [BLANK] of light.
5. Which of the following statements is true when you compare blue light (with a wavelength of 425nm) to orange light (with a wavelength of 620nm)
    a. orange light has a higher frequency and more energy than blue light
    b. blue light has a lower frequency than orange light

   c. orange light has a lower frequency but higher energy than blue light
   d. orange light has a lower frequency and less energy than blue light
   e. blue light has less energy than orange light

6. True or False? The formula $c=\lambda v$ can be used to solve for wavelength or frequency of electromagnetic radiation.

Check Your Answer[1]

Source: "Exercise 10.1a" by Jackie MacDonald, CC BY-NC-SA 4.0

Types of Electromagnetic Radiation (EMR)

We generally take light for granted, but it is a truly amazing and mysterious form of energy. Think about it: Light travels to Earth across millions of kilometres of empty space. When it reaches us, it interacts with matter in various ways to generate almost all the energy needed to support life, provide heat, and cause weather patterns. Light is a form of electromagnetic radiation (EMR). The term light usually refers to visible light, but this is not the only form of EMR. As we will see, visible light occupies a narrow band in a broad range of types of electromagnetic radiation.

Take a few minutes to study the positions of the various types of radiation on the EM spectrum in Figure 10.1c. Sometimes all radiation with frequencies lower than those of visible light are referred to as infrared (IR) radiation. This includes radio waves, which overlap with the frequencies used for media broadcasts of TV and radio signals. The microwave radiation that you see on the diagram is the same radiation that is used in a microwave oven or cell phone. What we feel as radiant heat is also a form of low-frequency EMR.

All the high-frequency radiation to the right of visible light is sometimes referred to as ultraviolet (UV) radiation. This includes X-rays and gamma (γ) rays. The narrow band that is visible light is a combination of the colours of the rainbow and extends from lower-frequency red light to higher-frequency violet light, thus the terms are infrared (below red) and ultraviolet (beyond violet).

Electromagnetic Radiation is typically classified by its wavelength.

TIPS for Success

Wavelengths of visible light are often given in nanometers, nm. One nm equals 10^{-9} m.

$$1 \text{ nm} = 10^{-9} \text{ m}$$

For example, yellow light has a wavelength of about 600 nm, or 6×10^{-7} m.

Listed below are several forms of electromagnetic radiation and its wavelength, in order from lowest frequency and energy to highest frequency and energy:

- Radiowaves = $\lambda > 0.01$ m.
- Microwaves = 10^{-4} m $< \lambda < 10^{-2}$ m
- Infrared (IR) = $8 \times 10^{-7} < \lambda < 10^{-5}$ m
- Visible = $4 \times 10^{-7} < \lambda < 8 \times 10^{-7}$ m (ROYGBIV – acronym for visible colour order)
- Ultraviolet (UV) = $10^{-8} < \lambda < 4 \times 10^{-7}$ m
- X-rays = $10^{-10} < \lambda < 10^{-8}$ m
- Gamma rays = $\lambda < 10^{-10}$ m

Example 10.1b

For the following example on types of electromagnetic radiation, reference Figure 10.1c.

Using the given five examples of electromagnetic radiation and its wavelength, arrange these in order of radiation that contains the most energy to least energy.

- Infrared **λ** = 900 nm
- Blue light = 450 nm
- Red light = 700nm
- Gamma rays **λ** = 0.01nM
- Radio waves **λ** = 3000 m

Solution

Since the wavelength of electromagnetic radiation is inversely proportional to its energy, they will be ordered from shortest wavelength to longest wavelength to show the order of radiation that contains most energy to least energy.

1. Gamma rays **λ** = 0.01nM – Contains the MOST ENERGY
2. Blue light = 450 nm
3. Red light = 700nm
4. Infrared **λ** = 900 nm

5. Radio waves λ = 3000 m – Contains the LEAST ENERGY

Source: “Example 10.1b” created by Jackie MacDonald, CC BY-NC-SA 4.0

Exercise 10.1b

For the following exercise, reference Figure 10.1c.

Using the given five examples of electromagnetic radiation and its wavelength, arrange these in order of radiation that has the lowest frequency to highest frequency.

- Microwaves = 300 cm
- Violet light = 400 nm
- Yellow light = 600nm
- X rays λ = 5 nm
- Infrared λ = 900 nm

Check Your Answer[2] Source: “Exercise 10.1b” created by Jackie MacDonald, CC BY-NC-SA 4.0

One can calculate the frequency or wavelength of electromagnetic radiation using the formula **c=λν**, where $c = 2.998 \times 10^8 \mathrm{ms}^{-1}$.

Example 10.1c

Calculations with Frequency and Wavelength of Electromagnetic Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1 × 10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the equation $c = \lambda v$ to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = (\frac{2.998 \times 10^{8}\ \cancel{\mathrm{m}}\mathrm{s}^{-1}}{589\ \cancel{\mathrm{nm}}})(\frac{1 \times 10^{9}\ \cancel{\mathrm{nm}}}{1\ \cancel{\mathrm{m}}}) = 5.09 \times 10^{14}\mathrm{s}^{-1}$$

Exercise 10.1c

Calculations with the Frequency and Wavelength of Electromagnetic Radiation

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850. MHz (3 significant figures). What is the wavelength in meters of these radio waves?

Check Your Answer[3]

Particle-Wave Duality

We have long known that EM radiation is like a wave, capable of interference and diffraction. We now see that light can also be modelled as particles—massless photons of discrete energy and momentum. In 1905, Albert Einstein (1879-1955), developed a theory stating that light has a dual nature: Light acts not only as a wave, but also as a particle. As illustrated above when discussing visible light, each particle of light has a quantum of energy associated with it and is called a **photon.** We call this twofold nature the **particle-wave duality**, meaning that EM radiation has properties of both particles and waves. This may seem contradictory, since we ordinarily deal with large objects that never act like both waves and particles. An ocean wave, for example, looks nothing like a grain of sand. However, this so-called duality is simply a term for properties of the photon analogous to phenomena we can observe directly, on a macroscopic scale. If this term seems strange, it is because we do not ordinarily observe details on the quantum level directly, and our observations yield either particle-like or wave-like properties, but never both simultaneously.

Watch **Wave-Particle Duality and the Photoelectric Effect (3:55)**

Exploring Specific Types of Electromagnetic Radiation

Wireless Communication – Radio Waves

Wireless communication uses long radio waves to travel great distances to transmit their signals. Some forms of EMR that use radio waves (all with different wavelengths, frequencies and energy amounts) include, radio broadcasting, cellular networks, radar, satellite communication, remote controlled toys, and navigation and air traffic control (GPS).

Wireless Communication

Figure 10.1d WIRELESS COMMUNICATION: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce, CC BY 2.0; credit middle: modification of work by M.O. Stevens, CC BY 3.0; credit right: work by Gary Minnaert, PD)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum (Figure 10.1d). At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 10.1e). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

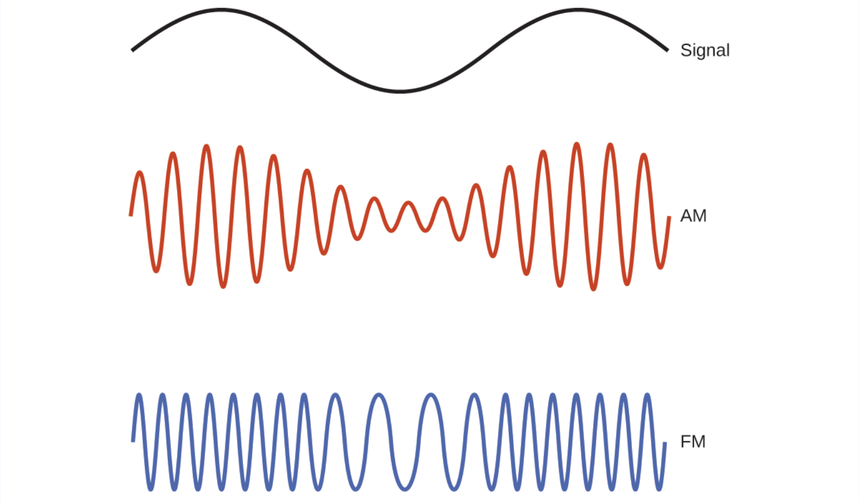


Figure 10.1e Schematic of AM and FM radio wave transmission**:** This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave. (credit: *Chemistry (Open Stax)*, CC BY 4.0).

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials. All are forms of radio waves.

X-Rays

X-Rays are a form of electromagnetic radiation, invisible to the human eye. Unlike visible light, x-rays have higher energy, higher frequency (and shorter wavelengths), which can penetrate most matter, including the body. Medical x-rays are used to generate images of tissues and structures inside the body.

Watch How Do X-rays Work? (1 min 28 s)

All of us can identify diagnostic uses of x-ray photons. Among these are the universal dental and medical x-rays that have become an essential part of medical diagnostics (Figure 10.1f and Figure 10.1g). X-rays are also used to inspect our luggage at airports, as shown in Figure 10.1h, and for early detection of cracks in crucial aircraft components. An x-ray is not only a noun meaning high-energy photon, it is also an image produced by x-rays, and it has been made into a familiar verb—to be x-rayed.

Figure 10.1f X-Ray of Human Mouth: An x-ray image reveals fillings in a person's teeth and can be use to detect cavities or other oral hygiene concerns. (credit: work by Dmitry G, PD)

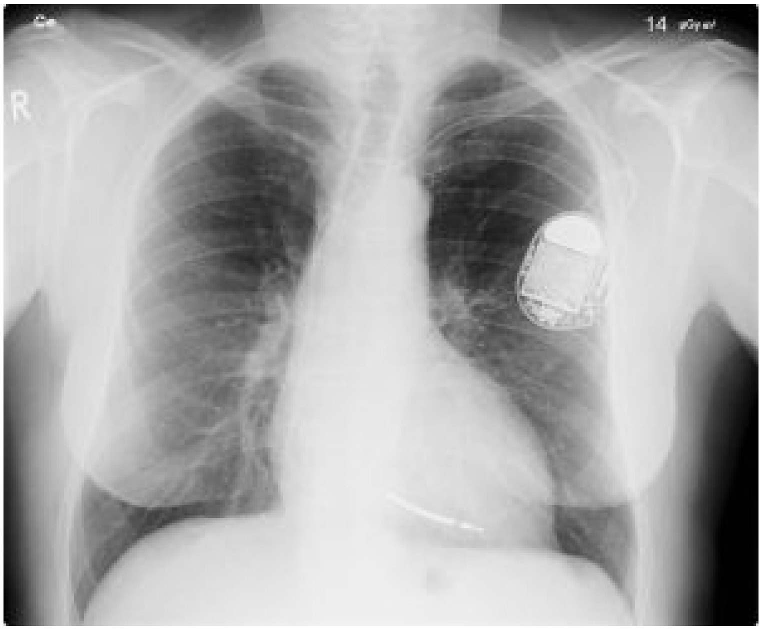


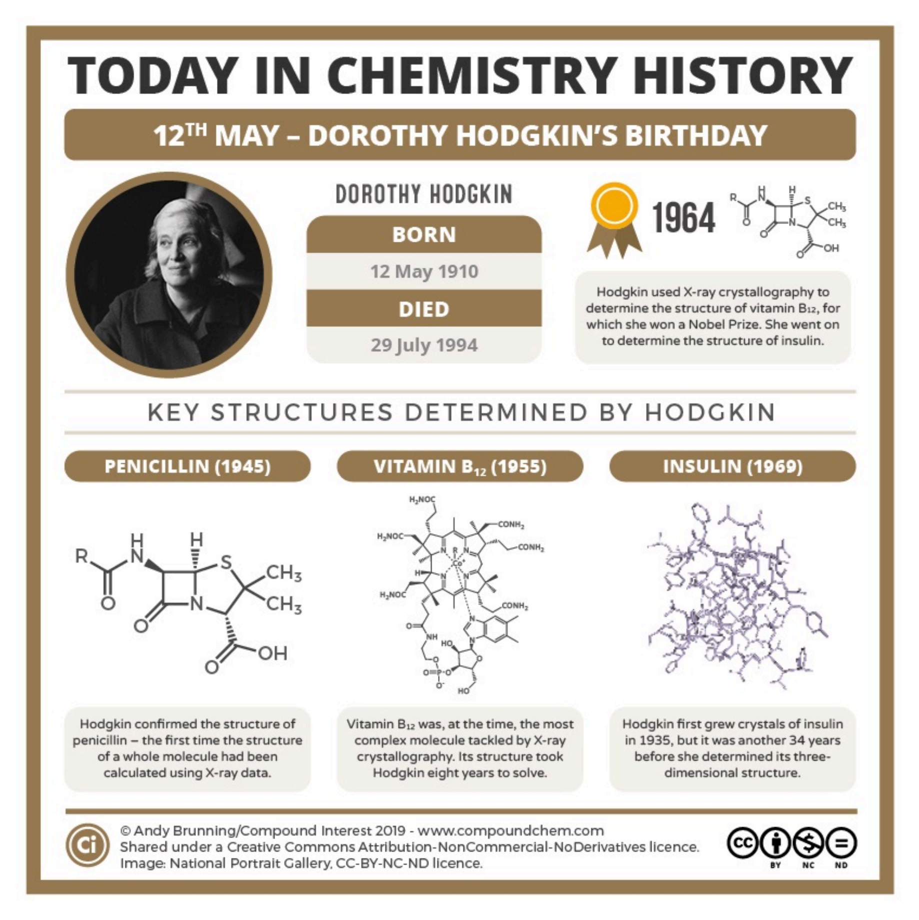
Figure 10.1g Medical Diagnostic Use of X-Ray: This x-ray image of a person's chest shows many details, including an artificial pacemaker. (credit: work by Sunzi99, CC BY 3.0)

Figure 10.1h X-Ray Imaging for Security: This x-ray image shows the contents of a piece of luggage. The denser the material, the darker the shadow. (credit: work by IDuke, CC BY 2.5)

The most common x-ray images are simple shadows. Since x-ray photons have high energies, they penetrate materials that are opaque to visible light. The more energy an x-ray photon has, the more material it will penetrate. So an x-ray tube may be operated at 50.0 kV for a chest x-ray, whereas it may need to be operated at 100 kV to examine a broken leg in a cast. The depth of penetration is related to the density of the material as well as to the energy of the photon. The denser the material, the fewer x-ray photons get through and the darker the shadow. Thus x-rays excel at detecting breaks in bones and in imaging other physiological structures, such as some tumours, that differ in density from surrounding material. Because of their high photon energy, x-rays produce significant ionization in materials and damage cells in biological organisms. Modern uses minimize exposure to the patient and eliminate exposure to others.

Scientists in Action: Dorothy Hodgkin, PhD.

Because the wavelengths of X-rays (10-10,000 picometres [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.



TODAY IN CHEMISTRY HISTORY

12TH MAY – DOROTHY HODGKIN'S BIRTHDAY

DOROTHY HODGKIN

BORN

12 May 1910

DIED

29 July 1994

1964

Hodgkin used X-ray crystallography to determine the structure of vitamin B12, for which she won a Nobel Prize. She went on to determine the structure of insulin.

KEY STRUCTURES DETERMINED BY HODGKIN

PENICILLIN (1945)

VITAMIN B12 (1955)

INSULIN (1969)

Hodgkin confirmed the structure of penicillin – the first time the structure of a whole molecule had been calculated using X-ray data.

Vitamin B12 was, at the time, the most complex molecule tackled by X-ray crystallography. Its structure took Hodgkin eight years to solve.

Hodgkin first grew crystals of insulin in 1935, but it was another 34 years before she determined its three-dimensional structure.

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Image: National Portrait Gallery, CC-BY-NC-ND licence.

Figure 10.1i Noble Prize Winner, Dorothy-Hodgkin: Dorothy Hodgkin was born on May 12, 1910; died July 29, 1994. She's most famous for being one of only four women to have won a Nobel Prize in Chemistry, and the only British woman to have done so. This graphic takes a look at the work that earned her the prize. She successfully determined the structure of penicillin in 1945, and in 1956 the structure of vitamin B12. Then in 1969 after over 30 years of capturing an x-ray photo of an insulin crystal , she determined insulin's three-dimensional structure. She used of X-ray crystallography to visualize the structures of molecules including penicillin, vitamin B12 and insulin. (credit:"This Day in Chemistry May 12 – Dorothy Hodgkin" by Andy Brunning/Compound Interest, CC BY-NC-ND 4.0)

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options. (Brunning, A., 2019)

Read more about Dorothy Crowfoot Hodgkin's Nobel Prize in Chemistry in 1964 [New Tab].

Key Equations

$c = \lambda\nu$

Attribution & References

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References

Brunning, A. (2019). This Day in Chemistry May 12 – Dorothy Hodgkin. *Compound Interest*. CC BY-NC-ND 4.0

Science Learning Hub – Pokapū Akoranga Pūtaiao, University of Waikato. (April 24, 2019). *Colours of Light*.

Notes

1. (1) True; (2) True; (3) True (4a) shorter, less; (4b) wavelength (λ); (4c) frequency (ν); (4d) longer, greater; (4e)

electromagnetic spectrum; (5) d; (6) True

2. Since the wavelength of electromagnetic radiation is inversely proportional to its frequency, they will be ordered from longest wavelength to shortest wavelength to show the order of radiation that contains lowest frequency to highest frequency.
    1. Microwaves = 300 cm - LOWEST FREQUENCY
    2. Infrared λ = 900 nm
    3. Yellow light = 600nm
    4. Violet light = 400 nm
    5. X rays λ = 5 nm - HIGHEST FREQUENCY
3. We can rearrange the equation $c = \lambda\nu$ to solve for the frequency:

$$\lambda = \frac{c}{\nu}$$

Since *c* is expressed in meters per second (ms^{-1}), we must also convert 850. MHz to s^{-1}. Recall, 1 MHz = 1.0×10^6 Hz = $1.0 \times 10^6\ s^{-1}$
So 850. MHz = $8.50 \times 10^8\ s^{-1}$
SOLVE:

$$\lambda = \frac{2.99 \times 10^8 ms^{-1}}{8.50 \times 10^8 s^{-1}}$$

λ = 0.3527 m (round final answer to 3 significant figures)
λ = 0.353 m

10.2 THE BOHR ATOM

Learning Objectives

By the end of this section, you will be able to:

- Explain the difference between the absorption spectrum and the emission spectrum of radiation emitted by atoms
- Describe the Bohr model of the hydrogen atom
- Summarize how Bohr's quantum model of the hydrogen atom explains the radiation spectrum of atomic hydrogen
- Review key equations used to calculate energies of light emitted or absorbed by hydrogen atoms

Our view of objects in the sky at night, the warm radiance of sunshine, the sting of sunburn, neon signs around us, our cell phone conversations, and the X-rays revealing a broken bone—all are brought to us by electromagnetic waves. It would be hard to overstate the practical importance of electromagnetic waves, through their role in vision, through countless technological applications, and through their ability to transport the energy from the Sun through space to sustain life and almost all of its activities on Earth.

Theory predicted the general phenomenon of electromagnetic waves before anyone realized that light is a form of an electromagnetic wave. In the mid-nineteenth century, James Clerk Maxwell formulated a single theory combining all the electric and magnetic effects known at that time. Maxwell's equations, summarizing this theory, predicted the existence of electromagnetic waves that travel at the speed of light. His theory also predicted how these waves behave, and how they carry both energy and momentum. These discoveries contributed to the emergence of the modern atomic theory.

Scientists continued to perform experiments to investigate the properties of electromagnetic radiation. Evidence supported that atoms could give off light. Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This theory was called the planetary model since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. Rutherford's model for atoms had one serious problem. Maxwell's theory of electromagnetic radiation says that when electrons change either speed or the direction of motion, they must emit energy. Science had proved that orbiting electrons constantly change their direction of motion, so they should, in theory, emit a constant stream of energy. Applying Maxwell's theory to Rutherford's model, all electrons should spiral into the nucleus of the atom as they lose energy, and this collapse should happen very quickly—in about 10^{-16} seconds. However, experimental results were not supporting such findings. Scientists concluded the atom's structure and how electrons move around the nucleus must be different than originally theorized. It was Danish physicist, Niels Bohr (1885–1962), who proposed an updated theory of how electrons remain in orbit.

Emission and Absorption Spectra

To understand the specifics of Bohr's model, we must first review the nineteenth-century discoveries regarding line spectra that prompted its formulation.

When we use a prism to analyze white light coming from the sun, several dark lines in the solar spectrum are observed (Figure 10.2a). Solar absorption lines are called Fraunhofer lines after Joseph von Fraunhofer, who accurately measured their wavelengths. During 1854–1861, Gustav Kirchhoff and Robert Bunsen discovered that for the various chemical elements, the line emission spectrum of an element exactly matches its line absorption spectrum. The difference between the absorption spectrum and the emission spectrum is explained in Figure 10.2b. An absorption spectrum is observed when light passes through a gas. This spectrum appears as black lines that occur only at certain wavelengths on the background of the continuous spectrum of white light (Figure 10.2b). The missing wavelengths tell us which wavelengths of the radiation are absorbed by the gas. The emission spectrum is observed when light is emitted by a gas. This spectrum is seen as colourful lines on the black background (Figure 10.2c and Figure 10.2d). Positions of the emission lines tell us which wavelengths of the radiation are emitted by the gas. Over time it was observed and concluded that each chemical element has its own characteristic emission spectrum. For each element, the positions of its emission lines are exactly the same as the positions of its absorption lines. This means that atoms of a specific element absorb radiation only at specific wavelengths and radiation that does not have these wavelengths is not absorbed by the element at all. This also means that the radiation emitted by atoms of each element has exactly the same wavelengths as the radiation they absorb.

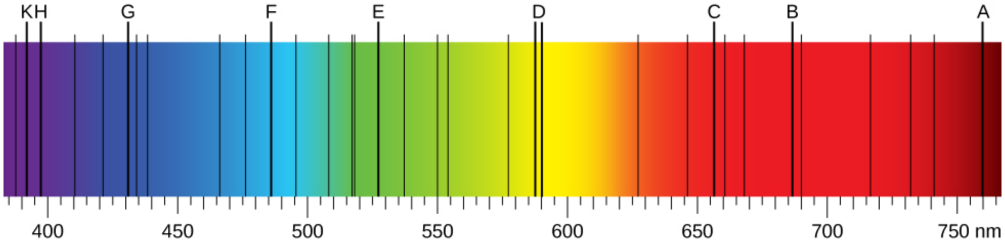

Figure 10.2a Absorption Spectra: In the solar emission spectrum in the visible range from 380 nm to 710 nm, Fraunhofer lines are observed as vertical black lines at specific spectral positions in the continuous spectrum. Highly sensitive modern instruments observe thousands of such lines. (credit: *University Physics Volume 3 (Open Stax)*, CC BY 4.0).

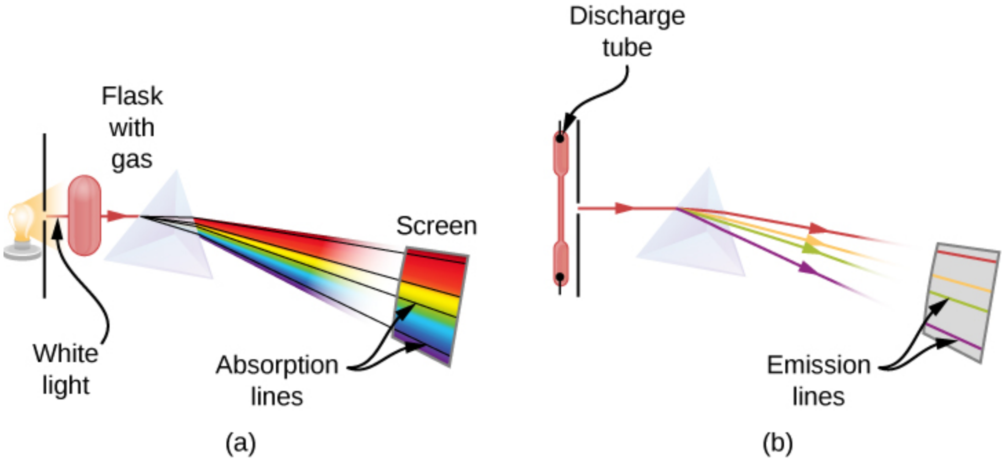

Figure 10.2b Observation of line spectra: (a) setup to observe absorption lines; (b) setup to observe emission lines. (a) White light passes through a cold gas that is contained in a glass flask. A prism is used to separate wavelengths of the passed light. In the spectrum of the passed light, some wavelengths are missing, which are seen as black absorption lines in the continuous spectrum on the viewing screen. (b) A gas is contained in a glass discharge tube that has electrodes at its ends. At a high potential difference between the electrodes, the gas glows and the light emitted from the gas passes through the prism that separates its wavelengths. In the spectrum of the emitted light, only specific wavelengths are present, which are seen as colourful emission lines on the screen. (credit: *University Physics Volume 3 (Open Stax)*, CC BY 4.0.)

Figure 10.2c The emission spectrum of atomic hydrogen: The spectral positions of emission lines are characteristic for hydrogen atoms. (credit: work by JKasd, CC BY 3.0)

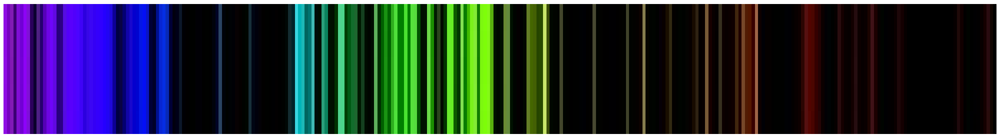

Figure 10.2d The emission spectrum of atomic iron: The spectral positions of emission lines are characteristic for iron atoms. (credit: *University Physics Volume 3 (Open Stax)*, CC BY 4.0.)

Emission spectra of the elements have complex structures; they become even more complex for elements with higher atomic numbers. The simplest spectrum, the emission spectrum of atomic hydrogen (Figure 10.2c), belongs to the hydrogen atom. Only four lines are visible to the human eye. As you read the emission spectrum of hydrogen from right to left, these lines are: red (656 nm), aqua (486 nm), blue (434 nm), and violet (410 nm). The lines with wavelengths shorter than 400 nm appear in the ultraviolet part of the spectrum and are invisible to the human eye. There are infinitely many invisible spectral lines in the series for hydrogen. Hydrogen's emission spectrum is much different than that of iron, which is shown in Figure 10.2d. It was determined that each element has a unique set of spectral lines that is characteristic of that element.

Watch Emission and Absorption Spectra (5:17)

The Bohr Atom

It was Niels Bohr who solved the mystery of how electrons remain in orbit. Historically, Bohr's model of the hydrogen atom is the very first model of atomic structure that correctly explained the specific radiation emittance spectra of atomic hydrogen. He applied the concept of energy quanta, proposed by German physicist, Max Planck (1858-1947), which stated that energy is never emitted continuously, but in small, discrete packages of energy called quanta. With this in mind, Bohr suggested that the spectrum of hydrogen can be understood if we assume that orbits of only certain sizes and specific distances from the atom's nucleus are possible for the electron to exist in. Bohr further assumed that as long as the electron moves in only one of these allowed orbits, it radiates no energy. Its energy would change only if it moved from one orbit to another. At the microscopic level of the atom, experiment after experiment has confirmed the validity of Bohr's strange idea. Bohr's suggestions became one of the foundations of the new (and much more sophisticated) model of the subatomic world called quantum mechanics.

In Bohr's model, if the electron moves from one orbit to another closer to the atomic nucleus, it must give up some energy in the form of electromagnetic radiation. If the electron goes from an inner orbit to one farther from the nucleus, however, it requires some additional energy. One way to obtain the necessary energy is to absorb electromagnetic radiation that may be streaming past the atom from an outside source.

A key feature of Bohr's model is that each of the permitted electrons that orbit around a given atom have a certain energy value; we, therefore, can think of each orbit as an energy level. Furthermore, all elements have the same set of energy levels. Lower energy levels are closer to the nucleus and higher energy levels are farther from the nucleus of an atom. To move from one orbit to another either up or down (which will have its own specific energy value) requires a change in the electron's energy—a change determined by the difference between the two energy values. Here we have one of the situations where it is easier to think of electromagnetic radiation as particles (photons) rather than as waves since each jump (or transition) to a different level has a fixed and definite energy change associated with it. Bohr concluded the following:

1. The atom must first receive a quantum amount of energy from an outside source for an electron to move to a higher orbit level and enters an **excited state** (an atom with excess energy).
2. When the excited electron moves to a lower energy level or its **ground state** (lowest possible state), the energy difference is released as a photon of light. The energy of the photon corresponds exactly to the energy change experienced by the emitting atom, which correlates with the colour of light specific to that energy amount.

A crude analogy for this situation might be life in a tower of luxury apartments where the rent is determined by the quality of the view. Such a building has certain, definite numbered levels or floors on which apartments are located. No one can live on floor 5.37 or 22.5. In addition, the rent gets higher as you go up to higher floors. If you want to exchange an apartment on the twentieth floor for one on the second floor, you will not owe as much rent. However, if you want to move from the third floor to the twenty-fifth floor, your rent will increase. In an atom, too, the "cheapest" place for an electron to live is the lowest possible level, and energy is required to move to a higher level.

The photon and wave perspectives must be equivalent: light is light, no matter how we look at it. Thus, each photon carries a certain amount of energy that is proportional to the frequency (f) of the wave it represents. The value of its energy (E) is given by the formula

$$E=hf$$

where the constant of proportionality, h, is called Planck's constant.

The constant is named for Max Planck, who was one of the originators of the quantum theory. If metric units are used (that is, if energy is measured in joules and frequency in hertz), then Planck's constant has the value $h = 6.626 \times 10^{-34}$ joule-seconds (J-s). As mentioned in the previous section, higher-energy photons correspond to higher-frequency waves (which have a shorter wavelengths); lower-energy photons are waves of lower frequency (which have longer wavelengths).

For a summary about the Bohr model of the atom, **watch the video** **The Bohr Atom (6:20)**

The Mathematics and Physics involved in the Evolution of the Bohr Atom

Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom, Planck's ideas of quantization and Albert Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = |E_\mathrm{f} - E_\mathrm{i}| = h\nu = \frac{hc}{\lambda}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values for the angular momentum, energy, and orbit radius, Bohr assumed that only discrete values for these could occur (actually, quantizing any one of these would imply that the other two are also quantized). Bohr's expression for the quantized energies is:

$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, \ldots$$

In this expression, k is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

$$\Delta E = k(\frac{1}{n_1^2} - \frac{1}{n_2^2}) = \frac{hc}{\lambda}$$

or

$$\frac{1}{\lambda} = \frac{k}{hc}(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

which is identical to the Rydberg equation for $R_\infty = \frac{k}{hc}$. Johannes Rydberg developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant (1.097×10^7 m^{-1}).

$$\frac{1}{\lambda} = R_\infty(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

When Bohr calculated his theoretical value for the Rydberg constant R_{∞}, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that **Bohr's model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

One of the fundamental laws of physics is that matter is most stable with electrons filling the lowest possible energy levels, which are designated by the letter *n*, where *n* is a positive integer. The lowest principal energy level is *n* = 1 and increase in increments of 1 for each successive higher energy level. Thus, the electron in a hydrogen atom usually moves in the *n* = 1 orbit, the lowest energy orbit and is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher *n* value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. The lowest few energy levels are shown in Figure 10.2d. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 10.2e). In effect, an atom can "store" energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of energy, as the electron returns to its ground state (say, from *n* = 5 to *n* = 1), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from *n* = 5 to *n* = 4, emitting one quantum, then to *n* = 1, emitting a second quantum).

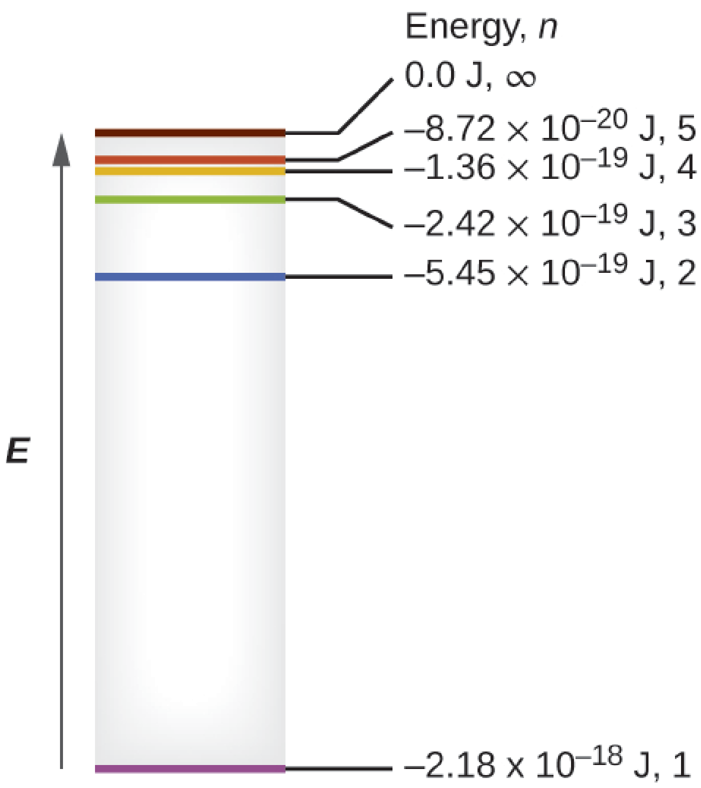

Figure 10.2e Quantum numbers and energy levels in a hydrogen atom: The more negative the calculated value, the lower the energy. (credit: *Chemistry (Open Stax)*, CC BY 4.0)

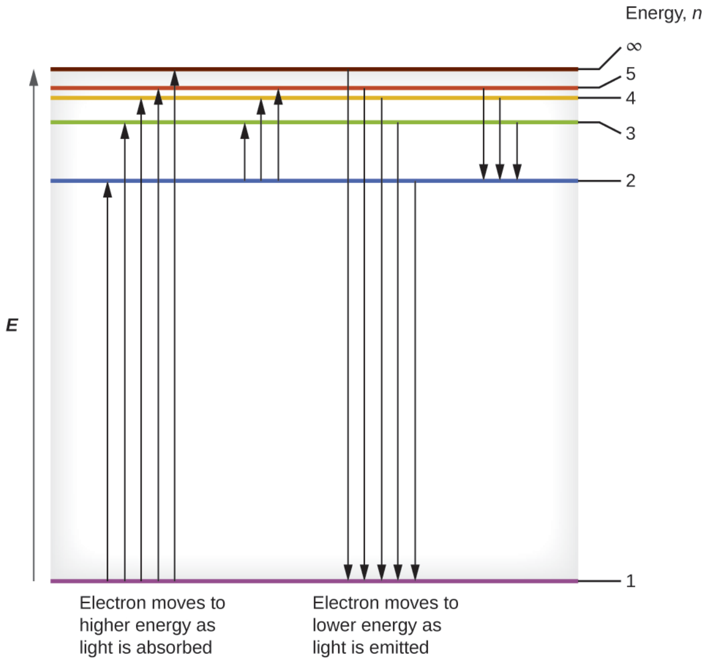

Figure 10.2f Relative energy of orbits in the Bohr model of the hydrogen atom: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits. (credit: *Chemistry (Open Stax)*, CC BY 4.0)

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^+, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which *Z* is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and *k* has a value of 2.179×10^{-18} J.

$$E_n = -\frac{kZ^2}{n^2}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which a_0 is a constant called the Bohr radius, with a value of 5.292×10^{-11} m:

$$r = \frac{n^2}{Z}a_0$$

The equation also shows us that as the electron's energy increases (as *n* increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence on *r* in the Coulomb potential, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases, and it is held less tightly in the atom. Note that as *n* gets larger and the orbits get larger, their energies get closer to zero, and so the limits $n \longrightarrow \infty$, and

$r \longrightarrow \infty$ imply that $E = 0$ corresponds to the ionization (energy) limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state $n = 1$, the ionization energy would be:

$$\Delta E = E_{n \longrightarrow \infty} - E_1 = 0 + k = k$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

For examples and exercises on applying these equations, visit section 6.2 – the Bohr Model In *Chemistry 2e* .

Watch Bohr Model of the Hydrogen Atom (4min 49s).

Exercise 10.2a

Check Your Learning Exercise (Text Version)
Part 1 Instructions: Review the scientist name list below. Match each of the nine scientists with their key discovery by filling in the [blank] with the correct scientist's name.

Scientist Name List (includes 9 names):

James Clerk Maxwell, Ernst Rutherford, Joseph von Fraunhofer, Gustav Kirchhoff, Robert Bunsen, Albert Einstein, Max Planck, Niels Bohr, Johannes Rydberg

Part 1 QUESTIONS:

1. [BLANK] accurately measured the wavelengths of solar absorption lines; these lines are named after the scientist who measured them.
2. [BLANK] developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range.

3. [BLANK] predicted the existence of electromagnetic waves that travel at the speed of light. His theory also predicted how these waves behave, and how they carry both energy and momentum.
4. [BLANK] theorized that electrons can move from one discrete energy level (orbit) to another by absorbing or emitting quantized energy.
5. [BLANK] is known as the originator of the quantum theory. Energy is never emitted continuously from an atom, but in small, discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.
6. [BLANK] and [BLANK] discovered that for the various chemical elements, the line emission spectrum of an element exactly matches its line absorption spectrum.
7. [BLANK] developed the planetary model of the nuclear atom since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus (protons and neutrons) like planets orbiting the sun.
8. [BLANK] determined that light consists of photons whose energy is proportional to their frequency.

Part 2 Instructions: Read the following statements about the Bohr atom and determine whether the statement is True OR False.

9. Bohr suggested that the spectrum of hydrogen can be understood if one assumes that orbits of only certain sizes and specific distances from the atom's nucleus are possible for the electron to exist in.
10. All electrons in an atom spiral into the nucleus of the atom as they lose energy.
11. Each element has a unique set of spectral lines that is characteristic of that element.
12. Lower energy levels are closer to the nucleus and higher energy levels are farther from the nucleus of an atom.
13. For an electron to move from a higher energy level to a lower energy level, it must absorb a discrete amount of energy from an outside source.
14. When an atom receives a quantum amount of energy from an outside source, it jumps to a higher orbit level and enters an excited state.
15. Matter is least stable when electrons fill the lowest possible energy levels.
16. The lowest principal energy level is n = 1 and increase in increments of 1 for each successive higher energy level.
17. When an electron transitions from an excited state to its ground state, the difference in energy is emitted as a photon.

Check Your Answer[1]

Source: "Exercise 10.2a" by Jackie MacDonald, licensed under CC BY-NC-SA 4.0

Bohr's model of the hydrogen atom provides insight into the behaviour of matter at the microscopic level, but it is does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases (becomes less stable) with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

Attribution & References

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(Open Stax)

Notes

1.
    1. Joseph von Fraunhofer;
    2. Johannes Rydberg;
    3. James Clerk Maxwell;
    4. Niels Boh;
    5. Max Planck;
    6. Gustav Kirchhoff and Robert Bunsen;
    7. Ernst Rutherford;
    8. Albert Einstein;
    9. True
    10. False;
    11. True;
    12. True;
    13. False;
    14. True;
    15. False;
    16. True;
    17. True

10.3 WAVE NATURE OF MATTER

Learning Objectives

By the end of this section, you will be able to:

- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

Wave Behaviour of Matter from a Microscopic Perspective

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behaviour of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patterns similar to those shown on Figure 10.3a. This is a case of wave behaviour on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

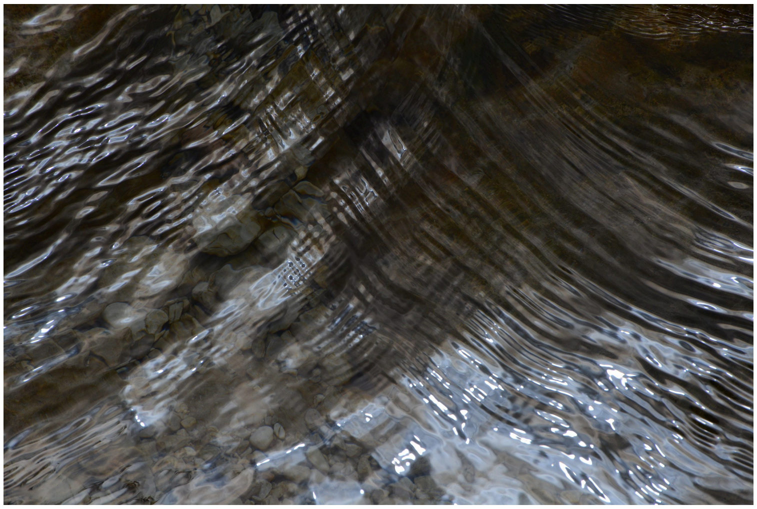


Figure 10.3a Interference Patterns on Water Surface: An interference pattern on the water surface is formed by interacting waves. The waves are caused by the reflection of water from the rocks. (credit: work by Daniela_deGol, CC BY 4.0)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behaviour of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behaviour of a wave with a wavelength value λ, given by this expression in which h is the familiar Planck's constant:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

This is called the *de Broglie wavelength*. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols are identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 10.3b).

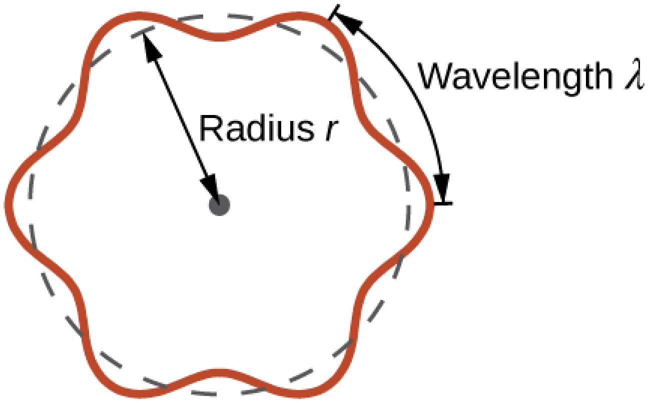


Figure 10.3b de Broglie's Electron Circulating Standing Wave Theory: If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behaviour to be possible (credit: *Chemistry (OpenStax)*, CC BY 4.0).

For a circular orbit of radius r, the circumference is $2\pi r$, and so de Broglie's condition is:

$$2\pi r = n\lambda, n = 1, 2, 3, \cdots$$

Since the de Broglie expression relates the wavelength to the momentum and, hence, velocity, this implies:

$$2\pi r = n\lambda = \frac{nh}{p} = \frac{nh}{mv} = \frac{nhr}{mvr} = \frac{nhr}{L}$$

This expression can be rearranged to give Bohr's formula for the quantization of the angular momentum:

$$L = \frac{nh}{2\pi} = n\hbar$$

Classical angular momentum L for a circular motion is equal to the product of the radius of the circle and the momentum of the moving particle p (Figure 10.3c).

$$L = rp = rmv \text{ (for a circular motion)}$$

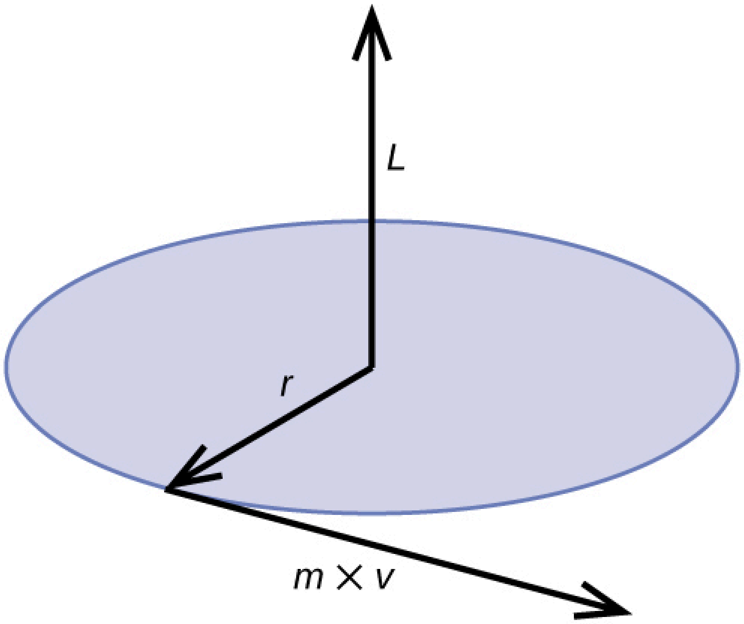
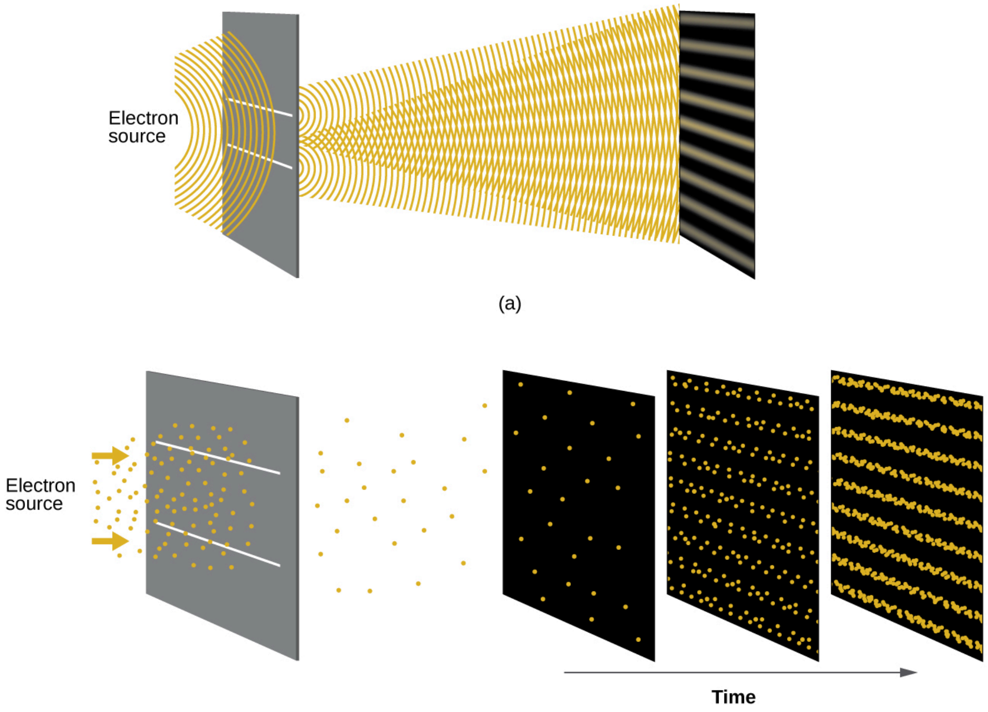


Figure 10.3c Angular Momentum for Circular Motion: The diagram shows angular momentum for a circular motion. L = rp = rmv (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behaviour by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 10.3d shows an interference pattern.



(a)

(b)

Figure 10.3d Experiments Showing Interference Pattern for Electrons (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behaviour. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. The electrons pass through very closely spaced slits, forming an interference pattern, with increasing numbers of electrons being recorded from the left image to the right. With only a few electrons recorded, it is clear that the electrons arrive as individual localized "particles," but in a seemingly random pattern. As more electrons arrive, a wavelike interference pattern begins to emerge. Note that the probability of the final electron location is still governed by the wave-type distribution, even for a single electron, but it can be observed more easily if many electron collisions have been recorded (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The wave–particle duality of matter can be seen in Figure 10.3d by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behaviour, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behaviour emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron's motion. Thus the wave–particle duality first observed with photons is actually a fundamental behaviour intrinsic to all quantum particles.

Watch Dr. Quantum – Double Slit Experiment (5min 12s)

Example 10.3a

Calculating the Wavelength of a Particle

If an electron travels at a velocity of 1.000 × 10^7 m s^{-1} and has a mass of 9.109 × 10^{-28} g, what is its wavelength?

Solution

We can use de Broglie's equation to solve this problem, but we first must do a unit conversion of Planck's constant. You learned earlier that 1 J = 1 kg m^2/s^2. Thus, we can write h = 6.626 × 10^{-34} J s as 6.626 × 10^{-34} kg m^2/s.

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34}\ \text{kg m}^2/\text{s}}{(9.190 \times 10^{-31}\ \text{kg})(1.000 \times 10^7\ \text{m/s})}$$

$$= \mathbf{7.274 \times 10^{-11}\ m}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behaviour is going to be noticeable in an atom.

Exercise 10.3a

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m s^{-1}, assuming that it can be modelled as a single particle.

Check Your Answer[1]

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the **Heisenberg uncertainty principle**: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. For a particle of mass m moving with velocity v_x in the x direction (or equivalently with momentum p_x), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x, must be greater than or equal to $\frac{\hbar}{2}$ (recall that $\hbar = \frac{h}{2\pi}$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position (Δx) has a value of, say, 1 pm (10^{-12} m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$[\Delta p = m\Delta v = \frac{h}{(2\Delta x)}] = \frac{(1.055 \times 10^{-34}\ \text{kg m}^2/\text{s})}{(2 \times 1 \times 10^{-12}\ \text{m})} = 5 \times 10^{-23}\ \text{kg m/s}$$

The value of $\hbar$ is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as $\Delta E\ \Delta t \geq \frac{\hbar}{2}$. Even the vector components of angular momentum cannot all be specified exactly simultaneously.

Watch **The Basics of Quantum Mechanics: What is the Heisenberg Uncertainty Principle? (4min 43s).**

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics. Recall that the equations of motion obtained from classical mechanics are trajectories where, at any given instant in time, both the position and the momentum of a particle can be determined exactly. Heisenberg's uncertainty principle implies that such a view is untenable in the microscopic domain and that there are fundamental limitations governing the motion of quantum particles. This does not mean that microscopic particles do not move in trajectories, it is just that measurements of trajectories are limited in their precision. In the realm of quantum mechanics, measurements introduce changes into the system that is being observed.

The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called wave–particle duality.

Attribution & References

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Notes

1. 1.9×10^{-34} m

10.4 QUANTUM MECHANICAL MODEL OF THE ATOM

Learning Objectives

By the end of this section, you will be able to:

- Understand the general idea of the quantum mechanical description of electrons in orbitals
- Relate the 3D shape of an orbital and how electrons are arranged within the atom to the radial distribution function
- List and describe traits of the four quantum numbers that describe orbitals and specify the location of an electron in an atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, as Bohr had argued, Erwin Schrödinger extended de Broglie's work by incorporating the de Broglie relation into a wave equation, deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra, and he did so without having to invoke Bohr's assumptions of stationary states and quantized orbits, angular momenta, and energies. Quantization in Schrödinger's theory was a natural consequence of the underlying mathematics of the wave equation. Like de Broglie, Schrödinger initially viewed the electron in hydrogen as being a physical wave instead of a particle, but where de Broglie thought of the electron in terms of circular stationary waves, Schrödinger properly thought in terms of three-dimensional stationary waves, or wavefunctions, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{\mathcal{H}}\psi = E\psi$$

$\hat{\mathcal{H}}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom), ψ is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

Watch **The Basics of Quantum Mechanics – What can Schrödinger's Cat Teach us about Quantum Mechanics? (5min 23sec).**

Watch **The uncertain location of elections (3:46 min)**
Video Source: TED-Ed. (2013, October 14). *The uncertain location of electrons – George Zaidan and Charles Morton* [Video]. YouTube.

Understanding Quantum Theory of Electrons in Atoms

Key discoveries about electron orbitals (location of electrons in atoms), their different energies, and other quantum properties led to our modern day understanding of atomic theory. The use of quantum theory provides the best understanding to these topics and provides the foundation to understanding why and how elements combine to form molecules through chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels. In atoms, an electrons location around the nucleus of an atom can be defined by four quantum numbers: the **principal quantum number** (n), the orbital **angular momentum quantum number** (l), the **magnetic quantum number (m_l)**, and the electron spin quantum number **(m_s)**.

Principal Quantum Number

The principal energy levels are labeled with an n value, where n = 1, 2, 3, …. Generally speaking, the energy of an electron in an atom is greater for greater values of n and as the n value increases, so does the distance from the nucleus of the atom. This number, n, is referred to as the principal quantum number. The principal quantum number defines the location of the energy level and is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The **spin quantum numbershells** of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure 10.4a). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

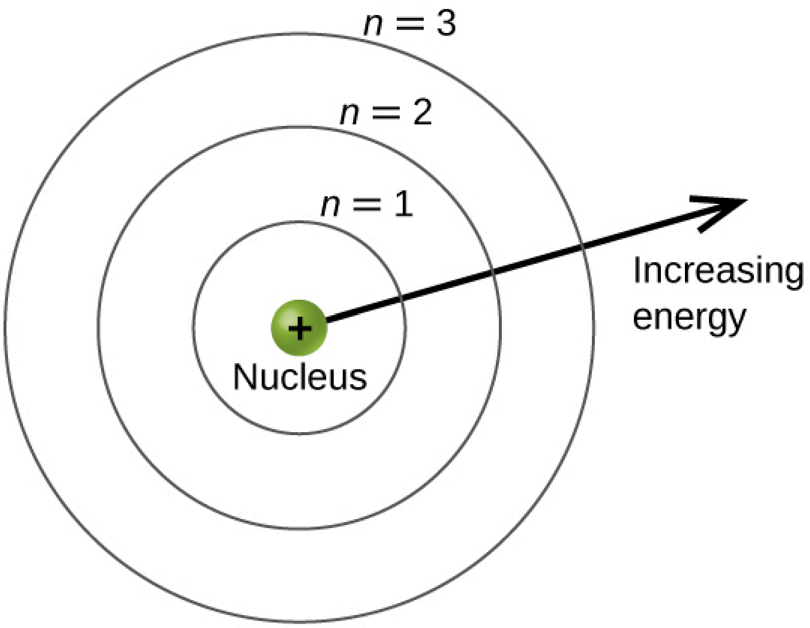

Figure 10.4a Principal Energy Level Schematic: Different shells are numbered by principal quantum numbers (credit: *Chemistry (OpenStax)*, CC BY 4.0).

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. As postulated by Bohr, if the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon of light is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the discrete energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18} (\frac{1}{n^2_\text{f}} - \frac{1}{n^2_\text{i}}) \;\text{J}$$

The values n_f and n_i are the final and initial energy states of the electron. To review calculations of such energy changes, see examples provided in *Chapter 10.2 – The Bohr Atom* .

The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital**, however, is distinct from Bohr's *orbit* analogy where the electron was thought to move around the nucleus in circular, defined orbits. Instead, and atomic orbital is a general region in an atom within which an electron is most probable to reside or be found in a given instant. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. It does not provide the precise path taken by an electron. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Angular Momentum Quantum Number

Another quantum number is l, the angular momentum quantum number. It is an integer that defines the shape of the orbital, and takes on the values, $l = 0, 1, 2, \ldots, n - 1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$ (one orbital shape), whereas $n = 2$ permits $l = 0$ and $l = 1$ (two orbital shapes) and so on. The principal quantum number defines the general size and energy of the orbital. The l value specifies the shape of the orbital. Orbitals with the same value of l form a **subshell**. In addition, the greater the angular momentum quantum number, the greater is the angular momentum of an electron at this orbital.

Orbitals with $l = 0$ are called ***s* orbitals** (or the *s* subshells). The value $l = 1$ corresponds to the *p* orbitals. For a given n, ***p* orbitals** constitute a *p* subshell (e.g., 3*p* if $n = 3$). The orbitals with $l = 2$ are called the ***d* orbitals**, followed by the $l = 3$, called the f orbitals. There are higher values we will not consider, as introductory chemistry courses typically focus on *s, p, d* and sometimes *f* orbitals.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wave function ψ is zero at this distance for this orbital. Such a value of radius r is called a radial node, which is the spherical surface region where the probability of finding an electron is zero. The number of radial nodes in an orbital is n – l – 1.

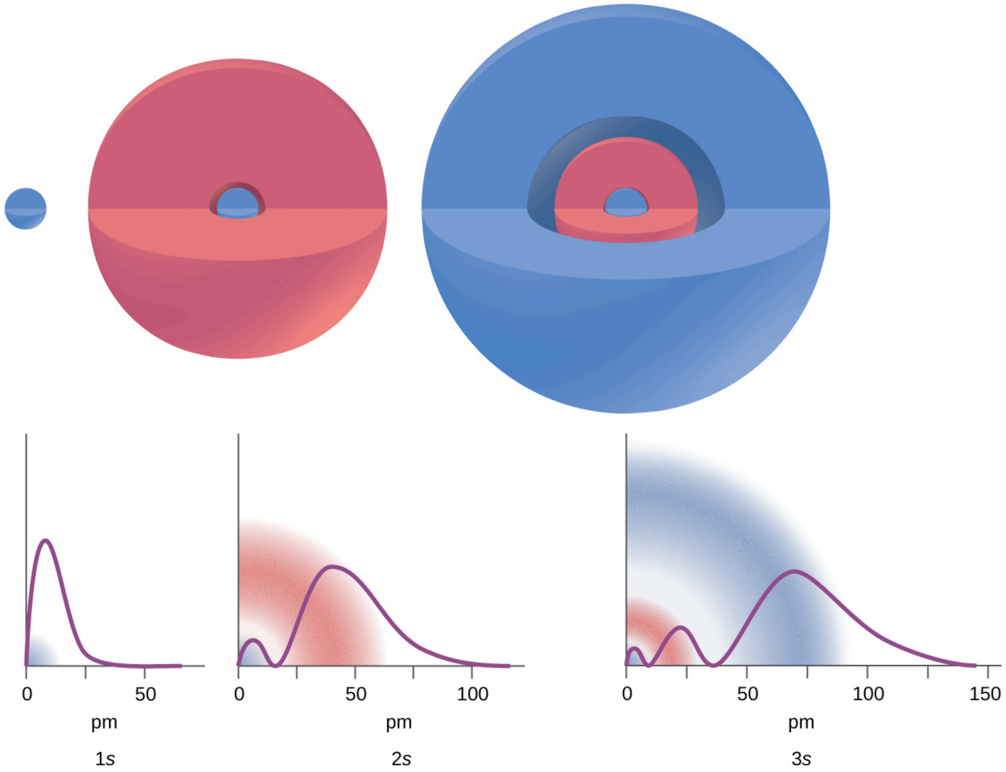

Figure 10.4b Probability of Finding an Electron vs Distance from Nucleus: The graphs show the probability (*y* axis) of finding an electron for the 1*s*, 2*s*, 3*s* orbitals as a function of distance from the nucleus (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Consider the examples in Figure 10.4b. The orbitals depicted are of the *s* type (which were determined to be sphere shaped probability orbital shapes), thus $l = 0$ for all of them. It can be seen from the graphs of the probability densities that for 1*s* ($n = 1$) there are 1 – 0 – 1 = 0 places where the density is zero (nodes). For 2*s* ($n = 2$) there are 2 – 0 – 1 = 1 node, and for the 3*s* orbitals (n = 3) there are 3 – 0 – 1 = 2 nodes.

It was determined that the *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found (Figure 10.4c).

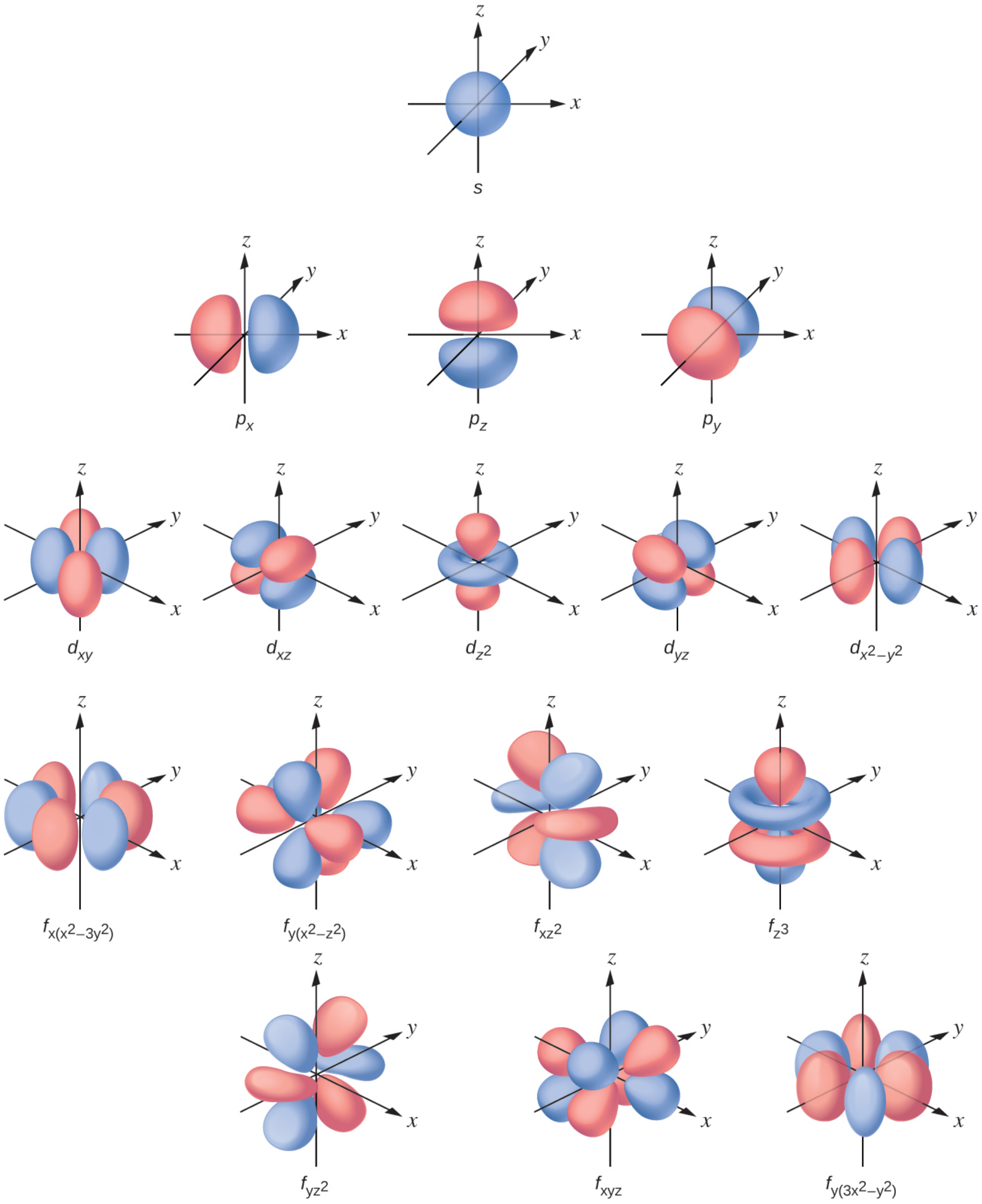

Figure 10.4c The Shapes of Orbitals: Shapes of *s*, *p*, *d*, and *f* orbitals (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If an electron has an angular momentum ($l \neq 0$), (as it will in *p*, *d*, *f* orbitals), then this vector can point in different directions. In addition, the *z* component of the angular momentum can have more than one value. This means that if a magnetic field is applied in the *z* direction, orbitals with different values of the *z* component of the angular momentum will have different energies resulting from interacting with the field. This provides the third quantum numbers, the magnetic quantum number, called m_l,

Magnetic Quantum Number

The magnetic quantum number (m_l) specifies the z component of the angular momentum for a particular orbital. For example, for an *s* orbital, $l = 0$, and the only value of m_l is zero. For *p* orbitals, $l = 1$, and m_l can be equal to -1, 0, or $+1$. Generally speaking, m_l can be equal to $-l, -(l - 1), \ldots, -1, 0, +1, \ldots, (l - 1), l$. The total number of possible orbitals with the same value of l (a subshell) is $2l + 1$. Thus, there is one *s*-orbital for $m_l = 0$, there are three *p*-orbitals for $m_l = 1$, five *d*-orbitals for $m_l = 2$, seven *f*-orbitals for $m_l = 3$, and so forth.

In summary, the principal quantum number defines the general value of the electronic energy, the angular momentum quantum number determines the shape of the orbital, and the magnetic quantum number specifies number of orientations of the orbital in space, as can be seen in Figure 10.4c.

Figure 10.4d illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, n. The letter in the orbital name defines the subshell with a specific angular momentum quantum number $l = 0$ for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$ (*p, d,* and *f* orbitals), each corresponding to a specific orientation, value of m_l. Figure 10.4d illustrates the concept of **degeneracy**, electron orbitals having the same energy levels. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same n are the same. In this case, the energy levels for the same principle quantum number, n, are called degenerate energy levels. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells in the same energy level have different energies, as shown on Figure 10.4d. For instance, an electron in the 2*s* orbital has lower energy than one in any of the three 2*p* orbitals. Orbitals of the same subshell (l value) are still degenerate and have the same energy (for example any of the three 2p subshells will have the same energy).

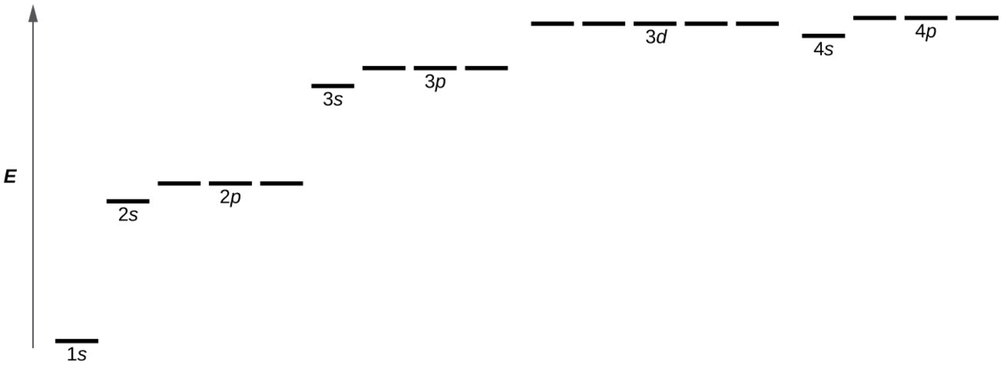

Figure 10.4d Energy Levels of Electron Orbitals: The chart shows the energies of electron orbitals in a multi-electron atom (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Spin Quantum Number

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the spin quantum number, or m_s.

The other three quantum numbers, n, l, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian x, y, and z). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, even though this rotation cannot be observed in terms of the spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number $m_s = \frac{1}{2}$. The other is called the β state, with the z component of the spin being negative and $m_s = -\frac{1}{2}$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = -\frac{1}{2}$ and $m_s = \frac{1}{2}$ are different if an external magnetic field is applied.

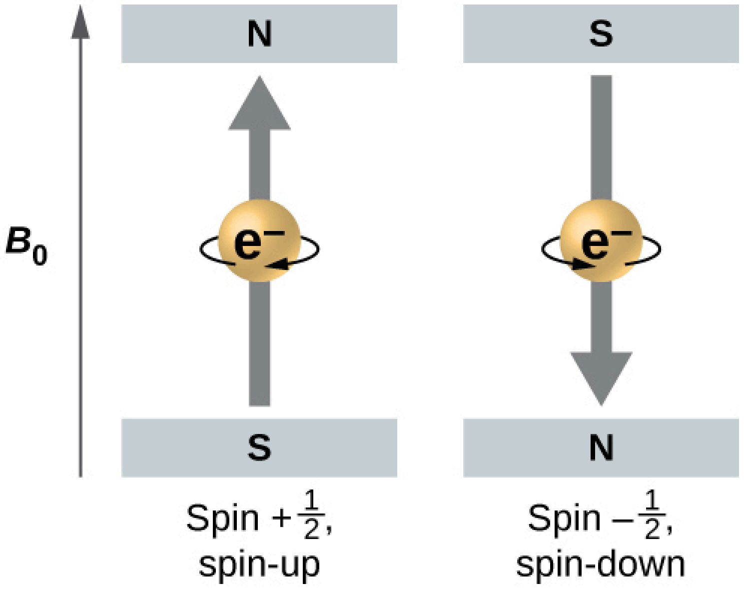

Figure 10.4e The Spin Quantum Number (m_s): Electrons with two possible spin values ±1/2 in an external magnetic field (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Figure 10.4e illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $\frac{1}{2}$ spin quantum number and down (in the negative *z* direction) for the spin quantum number of $-\frac{1}{2}$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on Figure 10.4e) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = \frac{1}{2}$ has a slightly lower energy in an external field in the positive *z* direction, and an electron with $m_s = -\frac{1}{2}$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behaviour of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers n, l, and m_l), but only if their spin quantum numbers, m_s, have different values. Since the spin quantum number can only have two values ($\pm\frac{1}{2}$), no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons.

The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 10.4a.

Table 10.4a Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital; principal energy level
angular momentum or azimuthal quantum number	l	$0 \le l \le n - 1$	subshell, the shape of the orbital (*s, p, d, f* ….)
magnetic quantum number	m_l	$- l \le m_l \le l$	orientation of the orbital
spin quantum number	m_s	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum "spinning" of the electron

The quantum (wave) mechanical model of the atom was devised. Electrons occupy orbitals, which are probability fields or spaces around the nucleus of an atom where an electron is likely to be found. Important criteria was established in developing this modern atomic theory:

1. Atoms have a series of energy levels called principal energy levels, which are designated by whole numbers (n = 1, 2, 3, ….).
2. The energy of the level increases as the value of n increases.
3. Each principal energy level contains one or more types of orbitals, called subshells.
4. The number of subshells present in a given principal energy level equals n. For example: Principal energy level 4 (n = 4) has 4 subshells including *s, p, d and f*
5. The n value is always used to label the orbitals of a given principal level and is followed by a letter that indicates the type (shape) of the orbital (For example: 1*s*, 2*p*, 3*d* ….).
6. An orbital can be empty or it can contain one or two electrons, but never more than two. If two electrons occupy the same orbital, they must have opposite spins.
7. The shape of an orbital does not indicate the specific details of electron movement (how it moves in a given orbital). It gives the probability distribution for where an electron is most likely to be found in that orbital.
8. The total number of orbitals in a given shell (principal energy level) is 2n and the maximum number of electrons in each shell (principal energy level) is $2n^2$.

The properties of the principal energy levels *(n* = 1-4), subshells, and capacity of electrons in each subshell and energy level is summarized in Table 10.4b.

10.4b Types of Orbitals and Electron Capacities of the First Four Principal Energy Levels

Principal Energy Level (n)	**Type of Subshell (l)**	**Number of Orbitals per Type of Subshell (m_l)**	**Orbital Name**	**Maximum Number of Electrons in each Subshell**	**Maximum Number of Electrons in each Principal Energy Level ($2n^2$)**
1	*s* (0)	1 (0)	1*s*	2	2
2	*s* (0)	1 (0)	2*s*	2	
2	*p* (1)	3 (-1, 0, +1)	2*p*	6	8
3	*s* (0)	1 (0)	3*s*	2	
3	*p* (1)	3 (-1, 0, +1)	3*p*	6	
3	*d* (2)	5 (-2, -1, 0, +1, +2)	3*d*	10	18
4	*s* (0)	1 (0)	4*s*	2	
4	*p* (1)	3 (-1, 0, +1)	4*p*	6	
4	*d* (2)	5 (-2, -1, 0, +1, +2)	4*d*	10	
4	*f* (3)	7 (-3, -2, -1, 0, +1, +2, +3)	4*f*	14	32

Source: "Table 10.4b" by Jackie MacDonald is licensed under CC BY-NC-SA 4.0.

For a video summary on quantum numbers and atomic orbitals as well as an introduction to electron orbital filling watch **Quantum Numbers, Atomic Orbitals, and Electron Configurations (8min 41s)**

Example 10.4a

Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the n = 4 shell of an atom. How many total orbitals are in principal energy level four (n = 4)

Solution

For n = 4, l can have values of 0, 1, 2, and 3. Thus, *s, p, d,* and *f* subshells are found in the n = 4 shell of an atom.

For l = 0 (the *s* subshell), m_l can only be 0. Thus, there is only one 4*s* orbital.

For l = 1 (*p*-type orbitals), m_l can have values of –1, 0, +1, so we find three 4*p* orbitals.

For $l = 2$ (*d*-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4*d* orbitals.

When $l = 3$ (*f*-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4*f* orbitals.

Thus, we find a total of (1+3+5+7) 16 orbitals in the $n = 4$ shell of an atom.

Exercise 10.4a

Working with Shells and Subshells

Identify the subshell in which electrons with the following quantum numbers are found: (a) $n = 3$, $l = 1$; (b) $n = 4$, $l = 3$; (c) $n = 2$, $l = 0$; (d) $n = 5$, $l = 0$; (e) $n = 3$, $l = 2$

Check Your Answer[1]

Example 10.4b

Maximum Number of Electrons – Electron Capacity

Calculate the maximum number of electrons that can occupy a shell with (a) $n = 2$, (b) $n = 4$, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When $n = 2$, there are four orbitals (a single 2*s* orbital, and three orbitals labeled 2*p*). Since a maximum of two electrons can occupy the same orbital, these four orbitals can contain eight electrons. (4 orbitals x 2 electrons in each orbital = 8 electrons).

(b) When $n = 4$, there are four subshells of orbitals that we need to sum:

$$\begin{array}{l}
\text{1 orbital labeled } 4s \\
\text{3 orbitals labeled } 4p \\
\text{5 orbitals labeled } 4d \\
\underline{\text{7 orbitals labeled } 4f} \\
\text{16 orbitals total}
\end{array}$$

Again, each orbital holds two electrons, so 32 electrons can fit in this $n = 4$ shell (32 electrons can fit in the fourth energy level)

Alternatively, one could use the formula $2n^2 = 2(4)^2 = 2(16) = 32$ electrons.

(c) The number of orbitals in any shell n will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$

Exercise 10.4b

Electron Capacity

Calculate the maximum number of electrons that can occupy a shell with

a. $n = 1$
b. $n = 5$

Check Your Answer[2]

Exercise 10.4c

Electron Capacity

If a shell contains a maximum of 32 electrons, what is the principal quantum number, n?

Check Your Answer[3]

Example 10.4c

Working with Quantum Numbers

Complete the following table for atomic orbitals using the following rules:

- The orbital designation is nl, where l = 0, 1, 2, 3, 4, ... is mapped to the letter sequence s, *p*, *d*, *f*, *g*, ...,
- The m_l degeneracy is the number of orbitals within an l subshell, and so is $2l + 1$ (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).

- The number of radial nodes is equal to $n – l – 1$.

Table 10.4c Working with Quantum Numbers Exercise 10.4c
Fill the spaces marked with blank in each column.

Orbital	n	l	m_l degeneracy	Radial nodes (no.)
4*f*	[blank]	[blank]	[blank]	[blank]
[blank]	4	1	[blank]	[blank]
[blank]	7	[blank]	7	3
5*d*	[blank]	[blank]	[blank]	[blank]

Solution

Table 10.4d ANSWERS to Exercise 10.4c Working with Quantum Numbers

Orbital	n	l	m_l degeneracy	Radial nodes (no.)
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Exercise 10.4d

How many orbitals have $l = 2$ and $n = 3$?

Check Your Answer[4]

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Notes

1.
    a. n = 3 is the third energy level, l - 1 represents p orbital ANSWER is 3p;
    b. n = 4 is the fourth energy level, l - 3 represents f orbital ANSWER is 4f;
    c. n = 2 is the second energy level, l - 0 represents s orbital ANSWER is 2s;
    d. n = 5 is the fifth energy level, l - 0 represents s orbital ANSWER is 5s;
    e. n = 3 is the third energy level, l - 2 represents d orbital ANSWER is 3d
2.
    a. $2n^2 = 2(1)^2 = 2$ electrons fill the first principal energy level (shell, n = 1);
    b. $2n^2 = 2(5)^2 = 50$ electrons fill the fifth principal energy level (shell, n = 5)
    c. ANSWER n = 4 follow these steps to solve: $2n^2 = 32$ (divide each side by two) $n^2 = 16$ (take the root of each side) n = 4; the fourth shell can has a capacity to fit 32 electrons
    d. the five degenerate 3d orbitals

10.5 ATOMIC STRUCTURES OF THE FIRST 20 ELEMENTS

Learning Objectives

By the end of this section, you will be able to:

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 10.5a depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing n value has more influence on energy than the increasing l value for small atoms. However, this pattern does not hold for larger atoms with more electrons The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

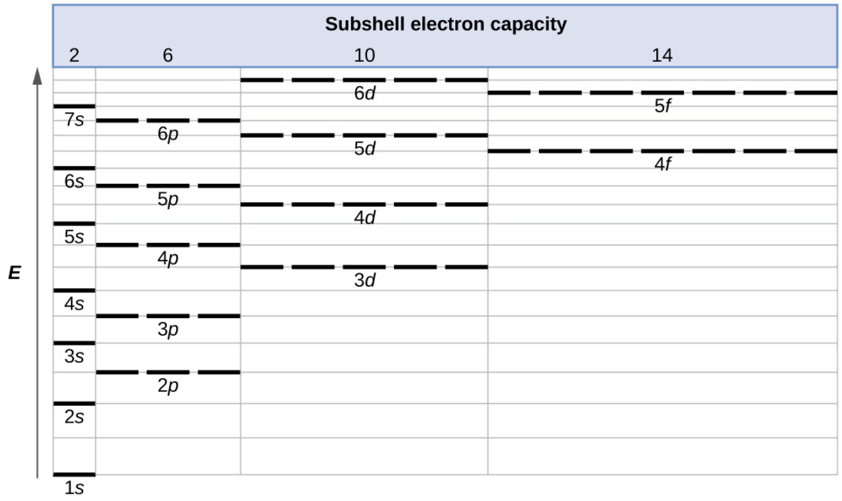


Figure 10.5a Generalized Energy-Level Diagram: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized), consistent with Coulomb's Law. But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is commonly represented using two methods: **orbital diagrams** and **electron configurations** of an atom. Both methods will be introduced in this section. It is important to apply the electron capacity rules for each type of subshell (*l*):

- electron capacity for subshell *s* is 2
- electron capacity for subshell *p* is 6
- electron capacity for subshell *d* is 10
- electron capacity for subshell *f* is 14

We write an electron configuration with a symbol that contains three pieces of information (Figure 10.5b):

1. The number of the principal energy level (shell), *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (*n*) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

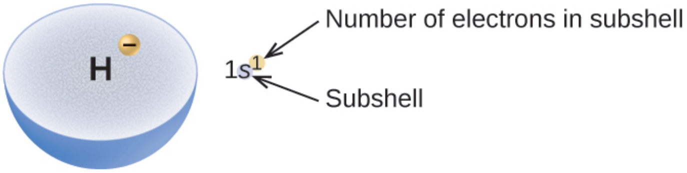


Figure 10.5b The diagram of an Electron Configuration for Hydrogen: The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The Aufbau Principle

To determine the electron configuration (electron filling order) for any particular atom, we can "build" the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* ("to build up"). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 10.5a), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 10.5c illustrates the traditional way to remember the filling order for atomic orbitals. It is a helpful schematic to use when writing electron configurations or drawing orbital diagrams.

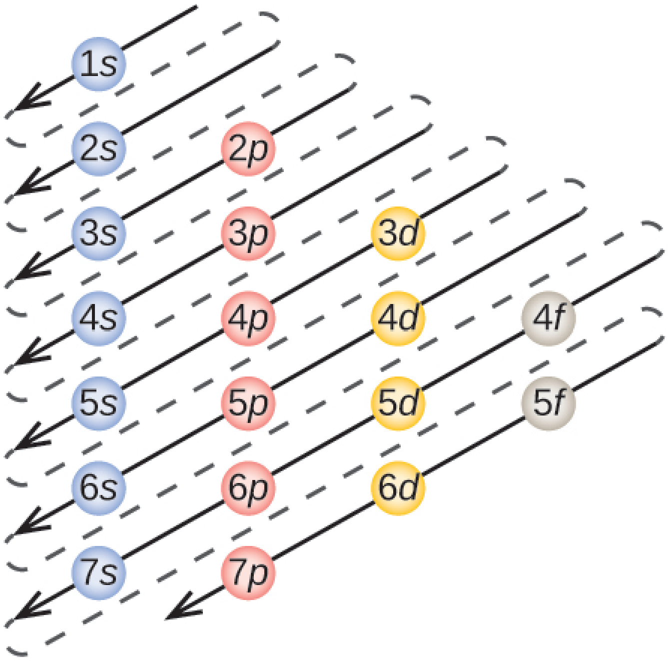


Figure 10.5c Using the Aufbau Principle to Determine Appropriate Filling Order for Electron Configurations: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown (credit: *Chemistry (OpenStax)*, CC BY 4.0).

For an introduction on how to use the Orbital Filling Diagram and Aufbau's principle to write electron configurations watch **Using the Electron Configuration Chart (3min 32s)**

Electron Configuration Arrangement using the Periodic Table

Since the arrangement of the periodic table is based on the electron configurations, the periodic table can be converted to an electron configuration table to map out electron filling order. Figure 10.5d illustrates this method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Argon (Ar), we see the next orbital to be filled with electrons will be 4s (for potassium (K) and calcium (Ca)), followed by the 3*d* orbitals.

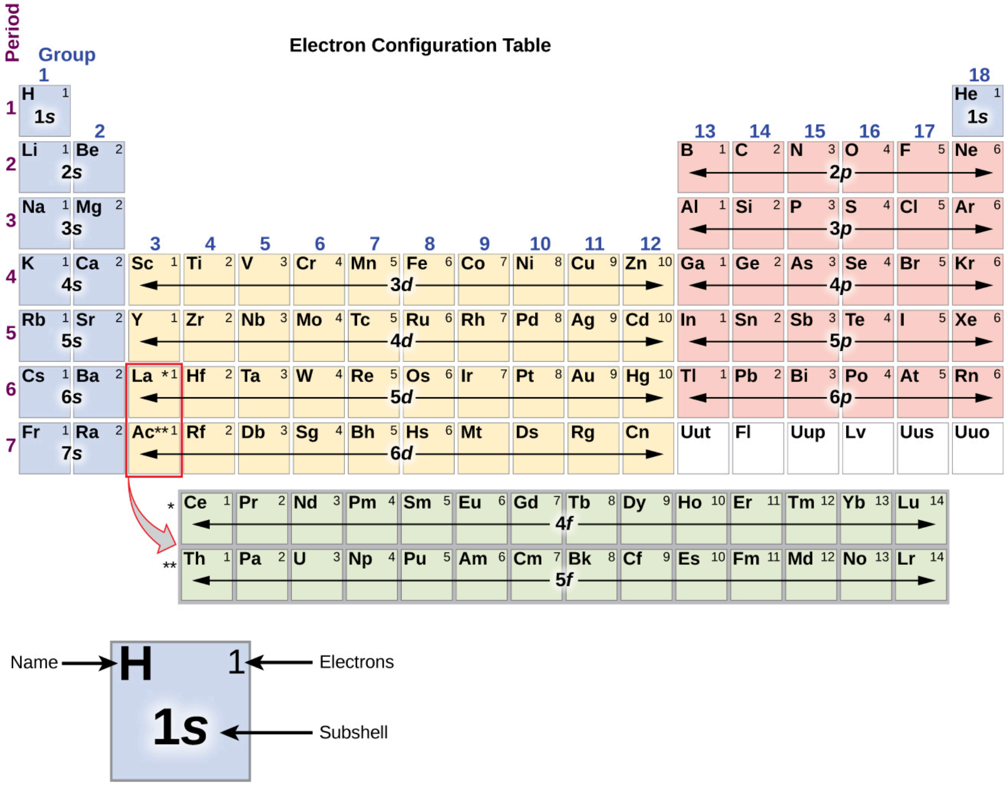


Figure 10.5d Using the Periodic Table to Predict Electron Configuration for each Subshell: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When filling electrons to create electron configurations and orbital diagrams, remember the number of electrons increases by one as the atomic number increases by one.

For an introduction on how to use the periodic table to write electron configurations, **watch Writing Electron Configurations Using Only the Periodic Table (4min 51s).**

Writing Electron Configuration and Orbital Diagrams of Elements

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. You can use the orbital filling diagram or your periodic table as tools to determine correct filling order. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. Boxes are drawn to represent each orbital (which can only contain zero, one, or two electrons). The orbitals' n value and l value are written under the box. Small arrows are used to indicate electrons. If two electrons share the same orbital, the first is drawn pointing in the up direction and the other in the down direction; this illustrates that the two electrons have opposite spins.

When reading orbital diagrams, you may notice two different version of arrows drawn: A full arrow head or "half" arrow head. Either is appropriate to use when drawing orbital diagrams, as both represent an electron. In this textbook, orbital diagrams will use both options interchangeably in examples, exercises, and answers.

We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 10.5c or Figure 10.5d, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The symbol for hydrogen, its electron configuration, and its orbital diagram, respectively, are:

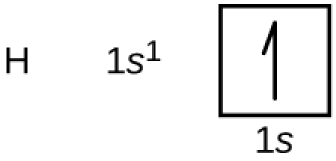


Figure 10.5e Electron configuration and orbital diagram for hydrogen (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accordance with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

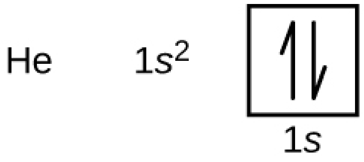


Figure 10.5f Electron configuration and orbital diagram for helium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The n = 1 shell is completely filled in a helium atom.

The next atom is the alkali metal lithium, with an atomic number of 3, which means it has three electrons to fill. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure 10.5c or Figure 10.5d). Thus, the electron configuration and orbital diagram of lithium are:

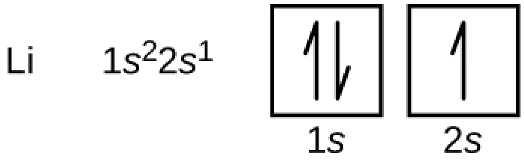


Figure 10.5g Electron configuration and orbital diagram for lithium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

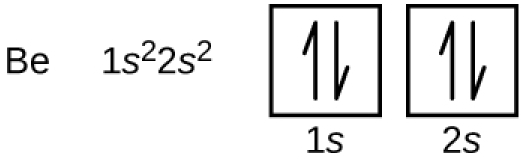


Figure 10.5h Electron configuration and orbital diagram for beryllium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

An atom of boron (atomic number 5) contains five electrons. The n = 1 shell is filled with two electrons and three electrons will occupy the n = 2 shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = −1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

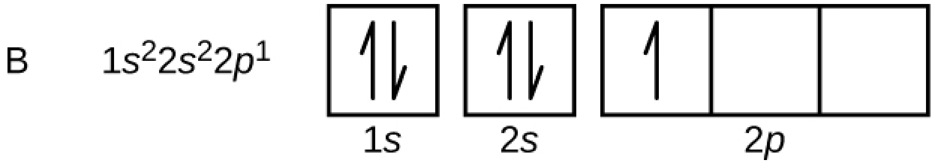


Figure 10.5i Electron configuration and orbital diagram for boron (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical *n*, *l*, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

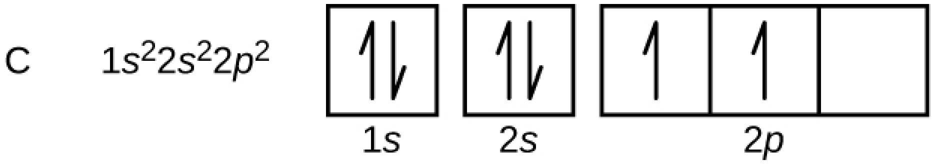


Figure 10.5j Electron configuration and orbital diagram for carbon (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule (electrons fill each orbital first, then double up). These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

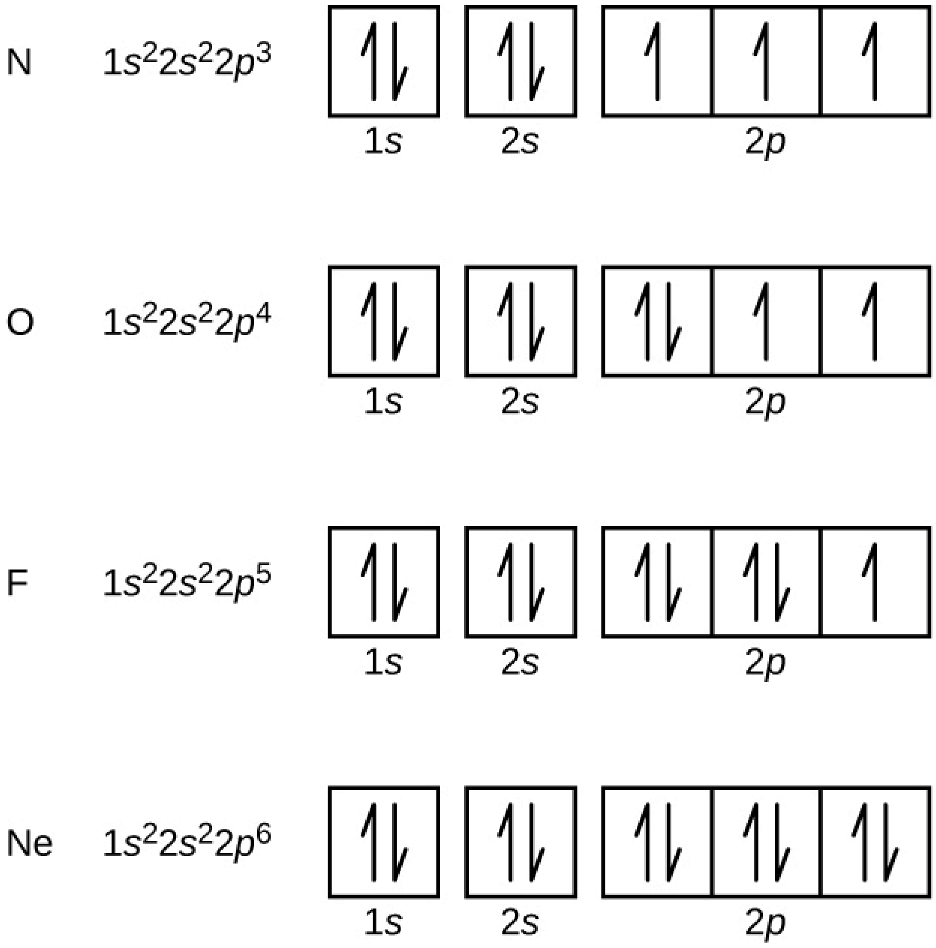


Figure 10.5k Electron configuration and orbital diagram for nitrogen, oxygen, fluorine, and neon (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the next lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 10.5e). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate and shorten electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. This is often referred to as the noble gas electron configuration of a given element. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[\text{Ne}]3s^1$.

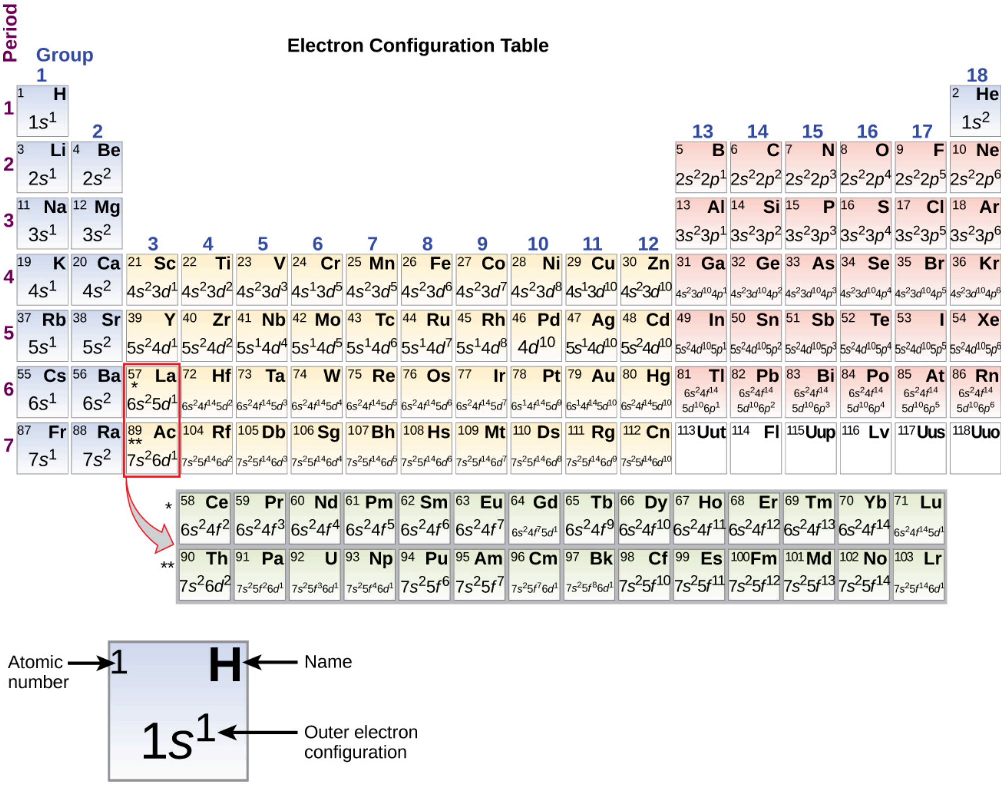
Figure 10.5l Identifying Core Electrons and Valence Electrons in Electron Configurations: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element. The abbreviated notation represents the elements noble gas electron configuration (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\begin{aligned}\text{Li} &: [\text{He}]\ 2s^1 \\ \text{Na} &: [\text{Ne}]\ 3s^1\end{aligned}$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^2 3p^1$, is analogous to its family member boron, [He]$2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 10.5m shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.



Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^5$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$	31 Ga $4s^23d^{10}4p^1$	32 Ge $4s^23d^{10}4p^2$	33 As $4s^23d^{10}4p^3$	34 Se $4s^23d^{10}4p^4$	35 Br $4s^23d^{10}4p^5$	36 Kr $4s^23d^{10}4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^14d^4$	42 Mo $5s^14d^5$	43 Tc $5s^14d^6$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$	49 In $5s^24d^{10}5p^1$	50 Sn $5s^24d^{10}5p^2$	51 Sb $5s^24d^{10}5p^3$	52 Te $5s^24d^{10}5p^4$	53 I $5s^24d^{10}5p^5$	54 Xe $5s^24d^{10}5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La * $6s^25d^1$	72 Hf $6s^24f^{14}5d^2$	73 Ta $6s^24f^{14}5d^3$	74 W $6s^24f^{14}5d^4$	75 Re $6s^24f^{14}5d^5$	76 Os $6s^24f^{14}5d^6$	77 Ir $6s^24f^{14}5d^7$	78 Pt $6s^14f^{14}5d^9$	79 Au $6s^14f^{14}5d^{10}$	80 Hg $6s^24f^{14}5d^{10}$	81 Tl $6s^24f^{14}5d^{10}6p^1$	82 Pb $6s^24f^{14}5d^{10}6p^2$	83 Bi $6s^24f^{14}5d^{10}6p^3$	84 Po $6s^24f^{14}5d^{10}6p^4$	85 At $6s^24f^{14}5d^{10}6p^5$	86 Rn $6s^24f^{14}5d^{10}6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac ** $7s^26d^1$	104 Rf $7s^25f^{14}6d^2$	105 Db $7s^25f^{14}6d^3$	106 Sg $7s^25f^{14}6d^4$	107 Bh $7s^25f^{14}6d^5$	108 Hs $7s^25f^{14}6d^6$	109 Mt $7s^25f^{14}6d^7$	110 Ds $7s^25f^{14}6d^8$	111 Rg $7s^25f^{14}6d^9$	112 Cn $7s^25f^{14}6d^{10}$	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

*	58 Ce $6s^24f^2$	59 Pr $6s^24f^3$	60 Nd $6s^24f^4$	61 Pm $6s^24f^5$	62 Sm $6s^24f^6$	63 Eu $6s^24f^7$	64 Gd $6s^24f^75d^1$	65 Tb $6s^24f^9$	66 Dy $6s^24f^{10}$	67 Ho $6s^24f^{11}$	68 Er $6s^24f^{12}$	69 Tm $6s^24f^{13}$	70 Yb $6s^24f^{14}$	71 Lu $6s^24f^{14}5d^1$
**	90 Th $7s^26d^2$	91 Pa $7s^25f^26d^1$	92 U $7s^25f^36d^1$	93 Np $7s^25f^46d^1$	94 Pu $7s^25f^6$	95 Am $7s^25f^7$	96 Cm $7s^25f^76d^1$	97 Bk $7s^25f^86d^1$	98 Cf $7s^25f^{10}$	99 Es $7s^25f^{11}$	100 Fm $7s^25f^{12}$	101 Md $7s^25f^{13}$	102 No $7s^25f^{14}$	103 Lr $7s^25f^{14}6d^1$

Figure 10.5m The Periodic Table showing the Outer-Shell Electron Configuration of each Element: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When we come to the next element in the periodic table we move down to period 4, group 1, the alkali metal potassium (atomic number 19). We might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level since it is the next lowest energy level (Figure 10.5m). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to its group 1 members, Li and Na in its valence shell configuration. The next element to consider is calcium. One electron is added to complete the 4*s* subshell and calcium has a

- complete electron configuration of $1s^22s^23p^64s^2$ and
- noble gas electron configuration of $[Ar]4s^2$

This gives calcium an outer-shell electron configuration corresponding to other elements in group 2 including beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n – 1)$ shell next to the *n* shell to bring that $(n – 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n – 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

For a summary on electron configurations and orbital filling diagrams **watch** **Electron Configuration (10min 16s).**

Example 10.5a

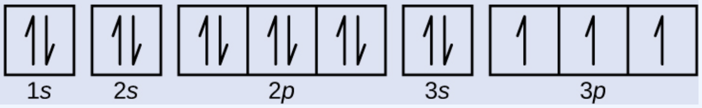
Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^22s^22p^63s^23p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 10.5a

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$
c. $1s^2 2s^2 2p^3$
d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

Check Your Answer[1]

Exceptions to Orbital Electron Filling Order

As mentioned previously in this section, the periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 10.5c or Figure 10.5d. For instance, the electron configurations (shown in Figure 10.5f) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

More about Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 10.5f), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behaviour of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 10.5m, which shows in periodic table form the electron configuration of the last subshell to be filled by the Aufbau principle. The coloured sections of Figure 10.5m show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell, or highest energy level orbitals of an atom.

1. Main group elements (sometimes called representative elements) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure 10.5m. This category includes all the nonmetallic elements, as well as many metals and the intermediate semi-metallic elements. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration $[\mathrm{Ar}]\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined – $4s^2$, $4p^1$). The completely filled *d* orbitals count as core, not valence, electrons.
2. Transition elements or transition metals. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and (*n* – 1) *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 10.5m) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (coloured yellow in Figure 10.5m), and we will adopt this usage in this textbook.
3. Inner transition elements are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 10.5m. The valence shells of the inner transition elements consist of the (*n* – 2)*f*, the (*n* – 1)*d*, and the *ns* subshells. There are two inner transition series:
    1. The lanthanide series: lanthanide (La) through lutetium (Lu)

2. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent (neutral) atom. For main group elements, the valence electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, valence electrons in the *s* orbital are easier to remove than the d or f electrons, and so the highest *ns* electrons are lost, and then the $(n - 1)d$ or $(n - 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to the valence shell of a parent atom. The added electrons fill in the order predicted by the Aufbau principle. Generally speaking:

- Metals forming simple cations typically lose valence electrons to achieve a stable electron configuration of their closest noble gas.
- Non-metals forming simple anions typically gain electrons to fill their outer valence shell to achieve a stable electron configuration of their closest noble gas.

Exercise 10.5b

Watch and Participate in this interactive video lesson (5min 11sec) to learn more about writing electron configurations of ions.

Check Your Learning Exercise (Text Version)
Question 1 (49 sec): For the two statements provided, fill in the [BLANK] with the correct key terms.

Key Terms:

1. gain; 2. lose; 3. cation; 4. Anion

Statements:

a. A positive ion is called a(n) [BLANK]. Atoms [BLANK] electrons to form this type of ion.

b. A negative ion is called a(n) [BLANK]. Atoms [BLANK] electrons to form this type of ion.

Question 2 (2min 8sec): Which of the following statements about calcium are true?

a. The electron configuration for neutral calcium atom is $1s^22s^22p^63s^23p^64s^2$
b. Calcium forms a Ca^{2+} cation by losing 2 electrons.
c. The electron configuration for a calcium 2+ ion is $1s^22s^22p^63s^23p^6$
d. a calcium 2+ ion has the same electron configuration as its closest noble gas, argon.
e. All these options are correct statements.

Questions 3 (2min 54sec) is a statement that reads, “This Lewis dot diagram is introducing concepts in ionic bonding of simple ions and is discussed in more detail in chemical bonding units”

Question 4 (3min 42sec) is a statement that reads, “The electron configuration of Al is incorrectly written in the video. The correct electron configuration of Al is $1s^22s^22p^63s^23p^1$.”

Question 5 (4min 7sec) is a statement that reads, “The three valence electrons lost from the aluminum atom were from $3s^23p^1$.”

Check Your Answer[2]

Activity Source: “Exercise 10.5b” by Jackie MacDonald is licensed under CC-BY-NC-SA 4.0, based on video source: Breslyn, W. (2020, October 1). *How to write the electron configuration for ions* [Video]. YouTube.

Example 10.5b

Predicting Electron Configurations of Ions

Write the electron configuration and orbital diagram of the following ions:

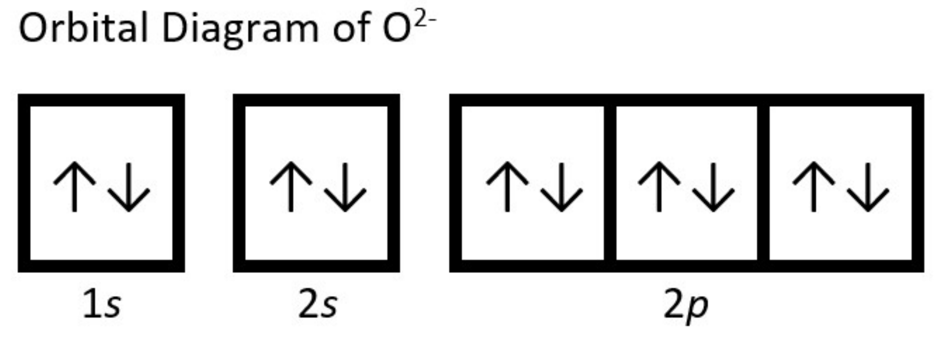
a. O^{2-}
b. Na^+
c. P^{3-}
d. Al^{2+}
e. Fe^{2+}

Solution

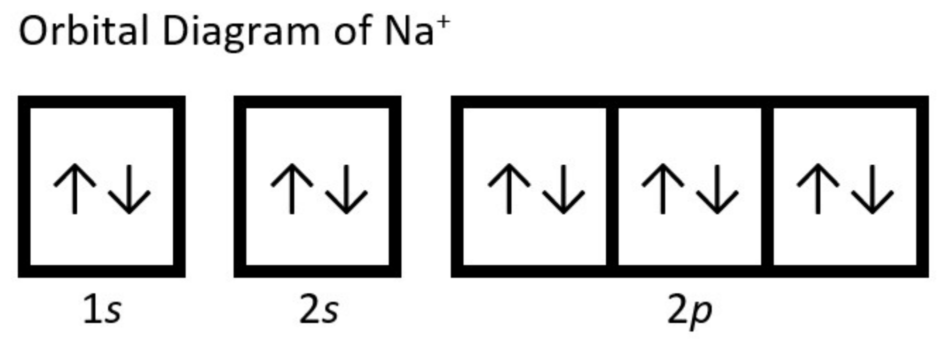
First, write out the electron configuration for each parent atom. We have shown full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

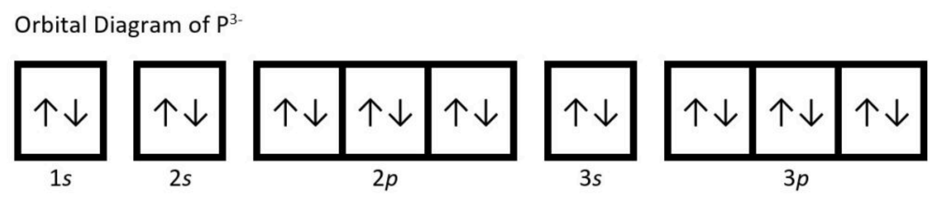
(a) O: $1s^22s^22p^4$. Oxygen anion gains two electrons in valence shell (2*p* shell), so O^{2-}: $1s^22s^22p^6$.



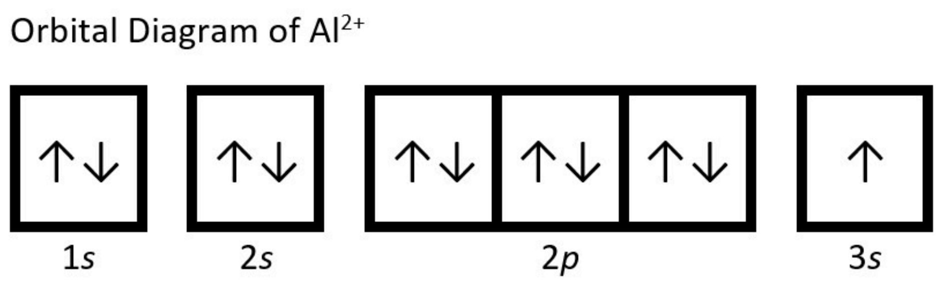
(b) Na: $1s^22s^22p^63s^1$. Sodium cation loses one electron from valence shell (3*s* shell), so Na^+: $1s^22s^22p^6$. To review a video showing the solution to this question watch Na$^+$ Electron Configuration (Sodium Ion) (2min 17s)



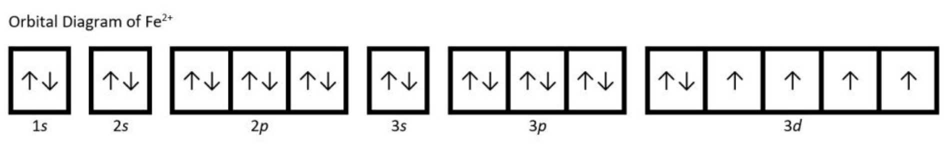
(c) P: $1s^22s^22p^63s^23p^3$. Phosphorus trianion gains three electrons (3 electrons are added to the valence shell, 3*p*) to form P^{3-}: $1s^22s^22p^63s^23p^6$.



(d) Al: $1s^22s^22p^63s^23p^1$. Aluminum dication loses two electrons (from outer valence shells; one from 3*p* and the other from 3*s*) to form Al^{2+}: $1s^22s^22p^63s^1$.



(e) Fe: $1s^22s^22p^63s^23p^64s^23d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital: Fe^{2+}: $1s^22s^22p^63s^23p^63d^6$.



Exercise 10.5c

Predicting Electron Configurations of Ions

1. Write the electron configuration and orbital diagram of the following ions:
   a. Mg^{2+}
   b. Cl^{-}
   c. Zn^{2+}
2. Which ion with a +2 charge has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^5$?

Which ion with a +3 charge has this configuration?

Check Your Answer[3]

Links to Interactive Learning Tools

Explore The Dynamic Periodic Table of Elements from Ptabla to reference noble gas electron configurations of elements.

Practice Electron configuration order from eCampusOntario H5P Studio.

Explore the It's Elementary section of The Interactive Periodic Table from Annenberg Learner.

Practice Electron Configurations from the Physics Classroom.

Attribution & References

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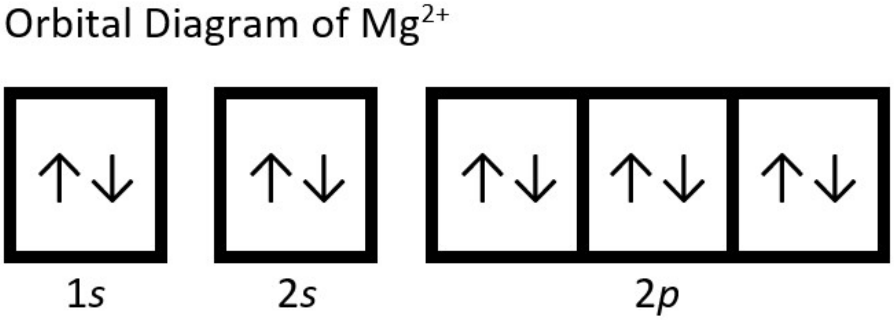
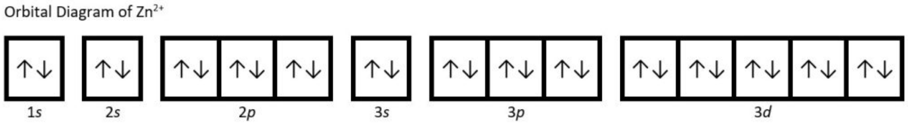
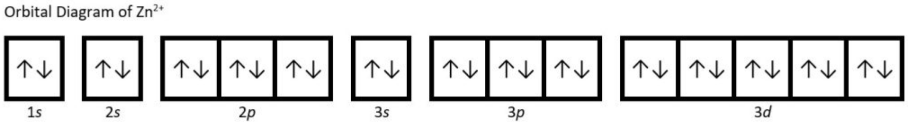
Notes

1.
    a. Mn;
    b. Xe;
    c. N;
    d. Br
2. Question 1: (a) cation, lose; (b) anion, gain
3. (1a) Mg^{2+}: $1s^22s^22p^6$





(1b) Cl^{-}: $1s^22s^22p^63s^23p^6$
(1c) Zn^{2+}: $1s^22s^22p^63s^23p^63d^{10}$



(2) Tc^{2+}, Ru^{3+}

10.6 ATOMIC PROPERTIES AND PERIODIC TABLE TRENDS

Learning Objectives

By the end of this section, you will be able to:

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements.

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behaviour. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colourless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behaviour. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

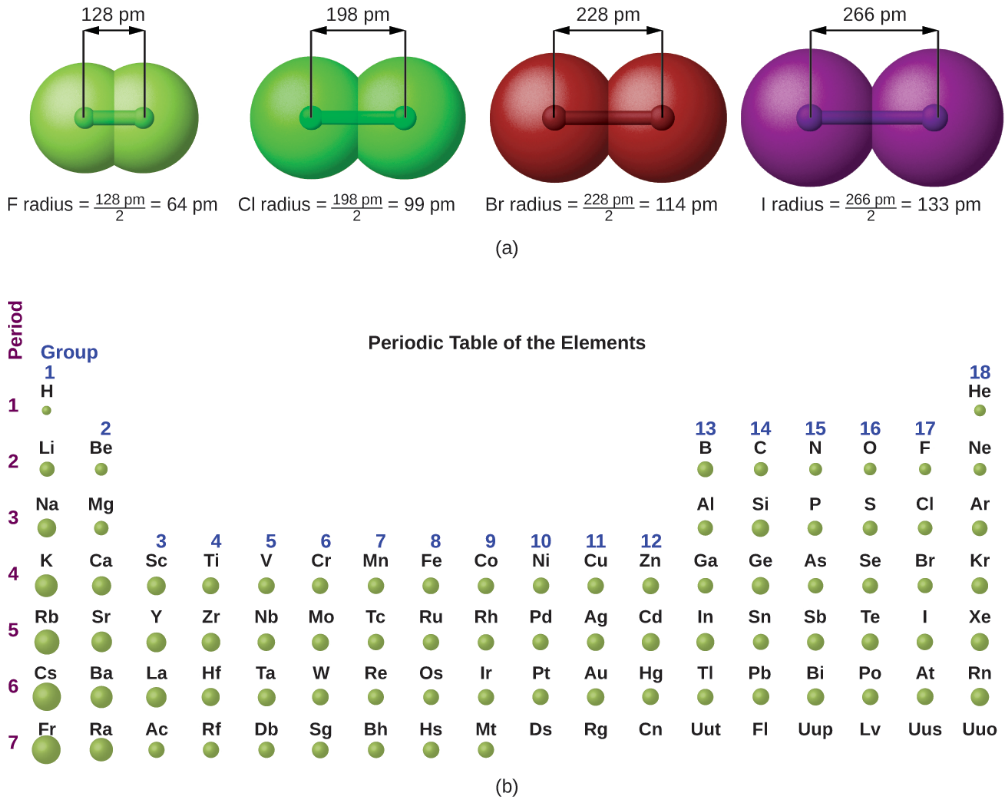
Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius** (Figure 10.6a), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 10.6a and Figure 10.6a (a). The trends for the entire periodic table can be seen in Figure 10.6a (b).

Table 10.6a Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure 10.6b, we see the general trend for atomic radii:



(a)

(b)

Figure 10.6a Trends in Atomic Radii using the Periodic Table: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. In (a) The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

As we move across a period from left to right, atomic radius decreases; as we move down a group the atomic radius increases.

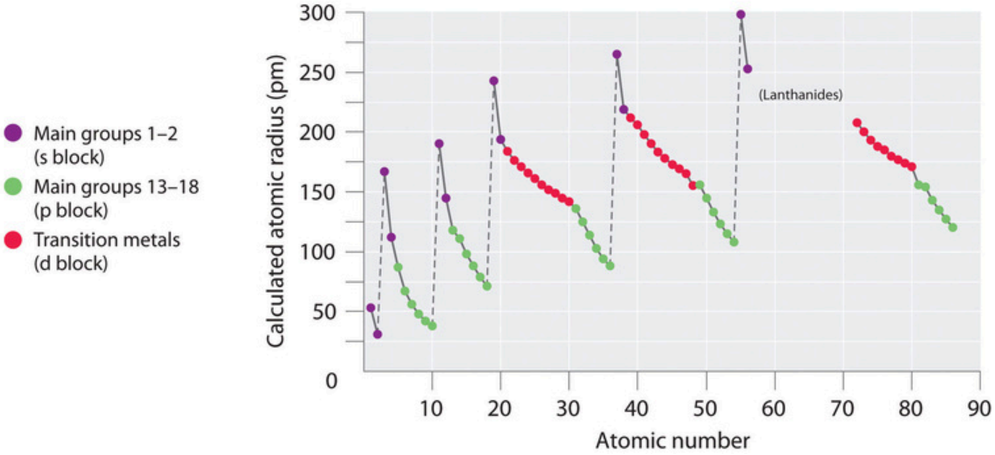


Figure 10.6b A Plot of Periodic Variation of Atomic Radius for the First Six Rows of the Periodic Table: The intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion. Atomic number is listed in ascending order on the x-axis. The calculated atomic radius (pm) is plotted on the y-axis. The main groups 1 and 2 (s Blocks) are shown in purple dots; the main groups 13-18 (p block) is shown in green dots; the transition metals (d block) are shown in red. The general trend shows that atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner. (credit: "7.3 Sizes of Atoms and Ions" by Joshua Halpern/LibreTexts, CC BY-NC-SA 4.0)

This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge, Z_{eff}**. This is the pull exerted on a specific electron by the nucleus, taking into account any electron-electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - shielding$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron-electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n-1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 10.6a

Sorting Atomic Radii using Periodic Table Trends

Predict the order of increasing covalent radius for Ge, Pb, Br, Kr.

Solution

Order of increasing covalent radius means ordering elements in order of smallest to largest Radii. Here, the radius increases as we move down a group, so Ge < Pb. Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Pb.

Exercise 10.6a

1. Give an example of an atom in group 2 whose size is larger than boron (B).
2. Predict the order of decreasing covalent radius for Mg, Fr, Cs, Na, Ca

Check Your Answer[1]

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 10.6c). For example, the covalent radius of an aluminum atom ($1s^22s^22p^63s^23p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^22s^22p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus and the cation is smaller than the parent atom.

Figure 10.6c Comparing Atomic Radius of a Cation to its Parent Atom: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 10.6c). For example, a sulfur atom ([Ne]$3s^2 3p^4$) has a covalent radius of 104 pm; whereas, the ionic radius of the sulfide anion ([Ne]$3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+}, which all have an electron configuration $1s^2 2s^2 2p^6$. Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+}, which all have an electron configuration([Ne]$3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Example 10.6b

Sorting Ionic Radii and Parent Atoms using Periodic Table Trends

Predict the order of increasing radius when comparing the following ions and parent atoms:

1. Mg^{2+} and Mg
2. N^{3-} and N
3. I^- and I
4. Cs^+ and Cs

Solution

Cations have smaller atomic radii than their parent atom; whereas, anions have larger atomic radii than their parent atom. We were asked to order by increasing radii, so smaller radii followed by larger radius.

1. Mg > Mg^{2+}
2. N^{3-} > N
3. I^{-} > I
4. Cs > Cs^{+}

Example 10.6c

Sorting Ionic Radii and Parent Atoms using Periodic Table Trends

Predict the order of decreasing atomic radius when comparing the following ions/atoms:

1. K^{+}, Ba^{2+}, F^{-}, K, Ba, F
2. Se^{2-}, Br^{-}, Kr, Rb^{+}, Sr^{2+}

Solution

Cations have smaller atomic radii than their parent atom; whereas, anions have larger atomic radii than their parent atom. We were asked to order by decreasing radii, so in order of largest radius to smallest radius.

1. Ba > Ba^{2+} > K > K^{+} > F^{-} > F
2. These ions all have the same electron configuration $[Ar]4s^{2}3d^{10}4p^{6}$ (the configuration of the noble gas Kr, [Kr]), and are said to be isoelectronic. For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge (# of protons), the smaller the radius in a series of isoelectronic ions and atoms. Therefore, largest to smallest we have: Se^{2-} > Br^{-} > Kr > Rb^{+} > Sr^{2+}

Exercise 10.6b

Predict the order of increasing atomic radius when comparing the following ions / atoms:

1. K^+, Cs^{2+}, O^{2-}, K, Fr, F^-
2. F^-, O^{2-}, Ne, Al^{3+}, Mg^{2+}

Check Your Answer[2]

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathrm{X}(g) \longrightarrow \mathrm{X}^+(g) + \mathrm{e}^- \qquad \mathbf{IE_1}$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X}^+(g) \longrightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^- \qquad \mathbf{IE_2}$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove.

Thus, as size (atomic radius) increases, the ionization energy should decrease.

Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period. Generally speaking, atomic radius and ionization energy are inversely proportional to one another.

Figure 10.6d graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 10.6d. Within a period, the IE_1 generally increases with increasing Z. Down a group, the IE_1 value generally decreases with increasing Z. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ($[\mathrm{He}]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[He]2s^2 2p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

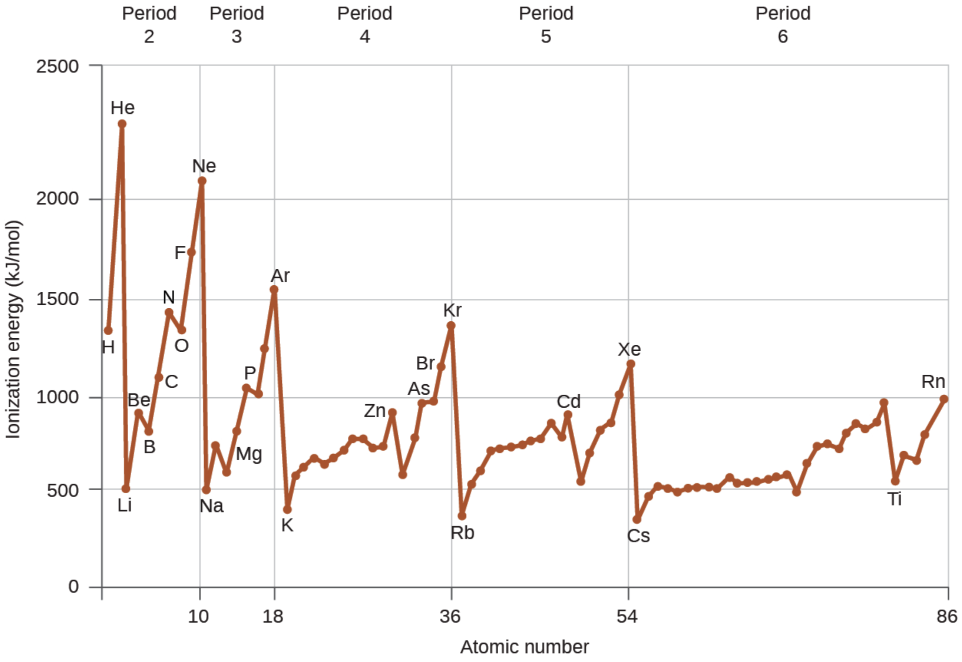
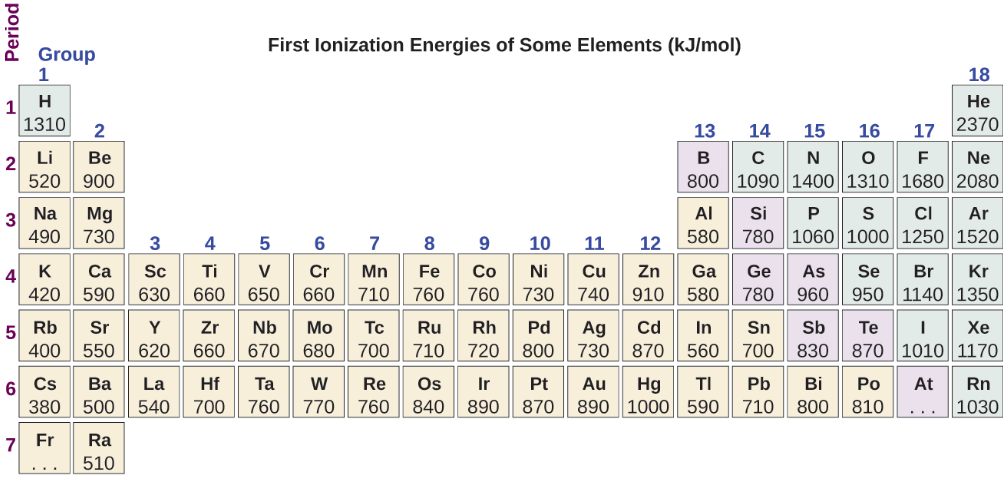


Figure 10.6d First Ionization Energies of Some Elements: The first ionization energy of the elements in the first five periods are plotted against their atomic number (credit: *Chemistry (OpenStax)*, CC BY 4.0).

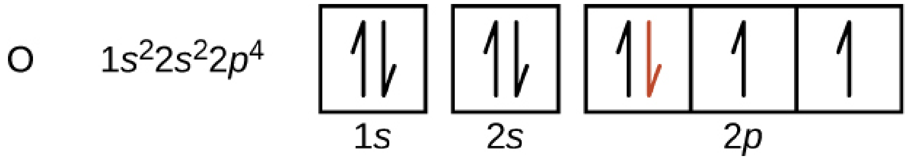


First Ionization Energies of Some Elements (kJ/mol)

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1310																	He 2370
2	Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At . . .	Rn 1030
7	Fr . . .	Ra 510																

Figure 10.6e Ionization Energies of Elements Shown in the Periodic Table: This version of the periodic table shows the first ionization energy of (IE_1), in kJ/mol, of selected elements. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron-electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favourable).



Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 10.6e).

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 10.6b, there is a large increase in the ionization energies (colour change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 10.6b Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example 10.6d

Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from Al ($Al^{2+} \rightarrow Al^{3+} + e^-$) requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: $IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na)$.

Exercise 10.6c

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Check Your Answer[3]

Variation in Electron Affinities

The **electron affinity** [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$\mathrm{X}(g) + \mathrm{e}^- \longrightarrow \mathrm{X}^-(g) \qquad \mathrm{EA}_1$$

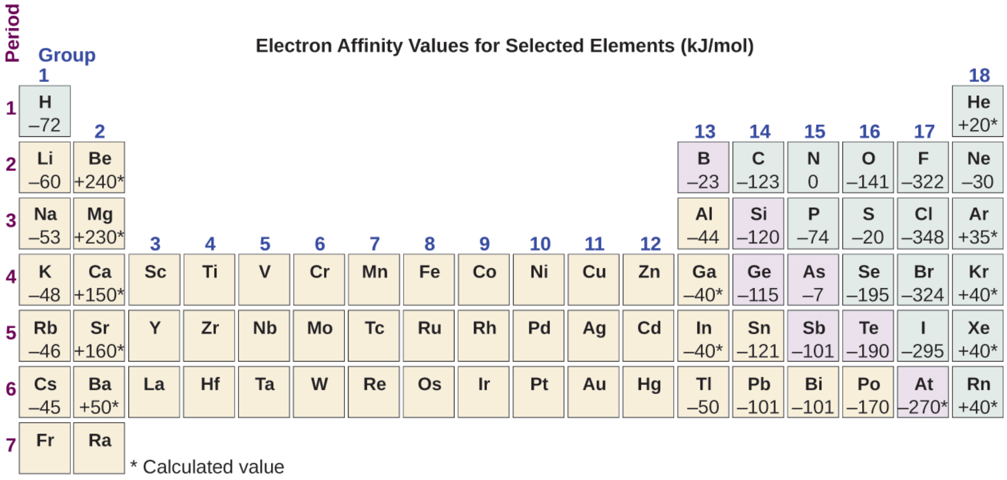
This process can be either endothermic (requiring energy) or exothermic (releasing energy), depending on the element. The EA of some of the elements is given in Figure 10.6f. You can see that some elements have negative values, whereas, other have positive values:

- Elements having negative values of EA tells us energy is released when the gaseous atom accepts an electron.
- Elements having positive values of EA means energy is required for the atom to become negatively charged.

Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron-electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron-electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.



Electron Affinity Values for Selected Elements (kJ/mol)

Period / Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H –72																	He +20*
2	Li –60	Be +240*											B –23	C –123	N 0	O –141	F –322	Ne –30
3	Na –53	Mg +230*											Al –44	Si –120	P –74	S –20	Cl –348	Ar +35*
4	K –48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga –40*	Ge –115	As –7	Se –195	Br –324	Kr +40*
5	Rb –46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In –40*	Sn –121	Sb –101	Te –190	I –295	Xe +40*
6	Cs –45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl –50	Pb –101	Bi –101	Po –170	At –270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure 10.6f Electron Affinities Shown in a Periodic Table: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

In summary, the electron affinity (EA) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are found in the upper right corner of the periodic table. With some exceptions to the rule, electron affinities become more negative across a row of the periodic table, which means they have a higher affinity for an electron. As you go down a group in the periodic table, atomic radius increases, ionization energy (affinity for their own valence electrons) decreases, and an atom's electron affinity for an added electron also decreases. Generally speaking,

> Electron affinity increases as you go up a group and from left to right across periods of the periodic table.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favourable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period is the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

For a summary on periodic table trends, **watch** **The Periodic Table: Atomic Radius, Ionization Energy, and Electronegativity (7 min 52 sec).**

Links to Interactive Learning Tools

Explore Periodictable.com's visualizations of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Practice Periodic Trends from the Physics Classroom.

Attribution & References

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Notes

1.
   1. possible answers include Be, Li
   2. Order of decreasing covalent radius means ordering elements in order of Largest to smallest Radii. Here, the radius increases as we move down a group, so Fr>Cs. Next determine which is the next largest radii by comparing Na, Mg and Ca. Radius decreases as we move across a period, so Mg>Na. Since radius increases as we move down a group Ca>Mg. Putting the trends together, we obtain Fr>Cs>Ca>Mg>Na.
2.
   1. $F^- < O^{2-} < K^+ < K < Cs^{2+} < Fr$;
   2. $Al^{3+} < Mg^{2+} < Ne < F^- < O^{2-}$
3. Ba has the lowest value for $1E_1$

CHAPTER 10 - SUMMARY

10.1 Electromagnetic Radiation

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998 × 10^8 m s^{-1}. This radiation shows wavelike behaviour, which can be characterized by a frequency (ν) and a wavelength (λ)such that $c = \lambda\nu$. Each particle of EMR spectrum has a quantum of energy associated with it and is called a photon. The energy of a photon is proportional to its frequency, and inversely proportional to its wavelength. Light demonstrates both wavelike and particle-like behaviour is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications.

10.2 The Bohr Atom

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. The colour of photon emitted will be specific to that photon's energy, frequency, and wavelength. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

10.3 Wave Nature of Matter

An electron possesses both particle and wave properties. The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called wave–particle duality. Louis de Broglie showed that the wavelength of particle is equal to Planck's constant divided by the mass times the velocity of the particle. He argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron's motion. Thus the wave–particle duality first observed with photons is actually a fundamental behaviour intrinsic to all quantum particles.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle.*

10.4 Quantum-Mechanical Model of the Atom

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n. Orbitals having the same value of n are said to be in the same shell. The angular momentum quantum number, l, can have any integer value from 0 to $n - 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principle quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l, with $2l + 1$ values ranging from $-l$ to $+l$, describes the orientation of the orbital in space. The forth quantum number is spin quantum number. Each electron has a spin quantum number, m_s, that can be equal to $(\pm\frac{1}{2})$. No two electrons in the same atom can have the same set of values for all the four quantum numbers. An orbital can be empty or it can contain one or two electrons, but never more than two. If two electrons occupy the same orbital, they must have opposite spins.

In summary, electrons occupy orbitals, which are probability fields or spaces around the nucleus of an atom where an electron is likely to be found. Important criteria was established in defining the modern atomic theory:

1. Atoms have a series of energy levels called principal energy levels, which are designated by whole numbers ($n = 1, 2, 3, ...$).
2. The energy of the level increases as the value of n increases.
3. Each principal energy level contains one or more types of orbitals, called subshells.
4. The number of subshells present in a given principal energy level equals n.
    1. For example: Principal energy level 4 ($n = 4$) has 4 subshells including *s, p, d and f*
5. The n value is always used to label the orbitals of a given principal level and is followed by a letter that indicates the type (shape) of the orbital (For example: 1*s*, 2*p*, 3*d* ....).
6. An orbital can be empty or it can contain one or two electrons, but never more than two. If two electrons occupy the same orbital, they must have opposite spins.
7. The shape of an orbital does not indicate the specific details of electron movement (how it moves in a given orbital). It gives the probability distribution for where an electron is most likely to be found in that orbital.
8. The total number of orbitals in a given shell (principal energy level) is $2n$ and the maximum number of electrons in each shell (principal energy level) is $2n^2$.

10.5 Atomic Structures of the First 20 Elements and the Periodic Table

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals). The orbital filling diagram and the periodic table can be used as tools to help determine the electron filling order when writing electron configurations and orbital diagrams. Full electron configuration or noble gas configurations can be used to represent the number of electrons in a parent atom. For ions, electron configurations and orbital diagrams can also be used to illustrate the electrons in an ion.

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behaviour of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

10.6 Atomic Properties and Periodic Table Trends

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher-energy orbital. Electron affinity (the energy associated with forming an anion) is more favourable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

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CHAPTER 10 - REVIEW

10.1 Electromagnetic Radiation & 10.2 The Bohr Atom

1. The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.
   Check Answer: [1]
2. The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?
   Check Answer: [2]
3. CKUN-FM is a First Nations/community radio station broadcasting at 101.3 FM dial in Christian Island, Ontario, Canada broadcasts at a frequency of $1.013 \times 10^{8}\ s^{-1}$ (101.3 MHz) (Wikipedia, 2022). What is the wavelength of these radio waves in meters?
   Check Answer: [3]
4. FM-95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^{7}\ s^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?
   Check Answer: [4]
5. A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapour. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?
   Check Answer: [5]
6. Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV ($1\ eV = 1.602 \times 10^{-19}\ J$)?
   Check Answer: [6]
7. Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the colour of the emitted light?
   Check Answer: [7]
8. A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the colour of the emitted light?
   Check Answer: [8]
9. When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What colour do we see when we heat a rubidium compound?

Check Answer: [9]

10. The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What colour are the lines?
    Check Answer: [10]
11. One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray? **Check Answer:** [11]
12. The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?
    Check Answer: [12]
13. RGB colour television and computer displays use cathode ray tubes that produce colours by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colours change. Using a spectrum of visible light, determine the approximate wavelength of each of these colours. What is the frequency and energy of a photon of each of these colours?
    Check Answer: [13]
14. Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of $n = 3$ than when it has a quantum number of $n = 1$?
    Check Answer: [14]
15. What does it mean to say that the energy of the electrons in an atom is quantized?
    Check Answer: [15]
16. Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Use formula $E_n = -\frac{kZ^2}{n^2}$ where Z is the nuclear charge (+1 for hydrogen) and k has a value of 2.179×10^{-18} J. Show your calculations.
    Check Answer: [16]
17. The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; 1 eV = 1.602×10^{-19} J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Use formula $\Delta E = k(\frac{1}{n_1^2} - \frac{1}{n_2^2})$ and k has a value of 2.179×10^{-18} J. Show your calculations.
    Check Answer: [17]
18. Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1, 2, 3$, and 4 orbits.
    Check Answer: [18]
    a. How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-

energy orbitals?

   b. Calculate the lowest and highest energies of light produced by the transitions described in part (a). Use formula $\Delta E = k(\frac{1}{n_1^2} - \frac{1}{n_2^2})$ and k has a value of 2.179 × 10–18 J.
   c. Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b). Using **Figure 10.1c: The Electromagnetic Spectrum** as a reference, specify the type of electromagnetic radiation emitted in each energy jump in part (b). Use E=hf to calculate frequency, where the constant of proportionality, h, is called Planck's constant h = 6.626×10^{-34} joule-seconds (J-s). Use equation c = λν to solve for the wavelength: $\lambda = \frac{c}{\nu}$

19. How are the Bohr model and the Rutherford model of the atom similar? How are they different?
   Check Answer: [19]
20. The spectra of hydrogen and of iron are shown in **Figures 10.2c and 10.2d Comparing Emission Line Spectra of White Light and Light from Various Elements**. When referencing these figures, recall that 1 angstrom = 0.1 nm = 1×10^{-10} m. Answer the following questions: (a) What causes the lines in these spectra? (b) Why are the colours of the lines different? (c) Suggest a reason for the observation that the spectrum of iron is more complicated than the spectrum of hydrogen.
   Check Answer: [20]

10.3 Wave Nature of Matter & 10.4 Quantum Mechanical Model of the Atom

1. How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?
   Check Answer: [21]
2. Summarize the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?
   Check Answer: [22]
3. Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.
   Check Answer: [23]
4. Identify the subshell in which electrons with the following quantum numbers are found:
   Check Answer: [24]
   a. $n = 2, l = 1$
   b. $n = 4, l = 2$
   c. $n = 6, l = 0$
5. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

Check Answer: [25]

6. Identify the subshell in which electrons with the following quantum numbers are found:
   Check Answer: [26]
   a. $n = 3, l = 2$
   b. $n = 1, l = 0$
   c. $n = 4, l = 3$
7. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?
   Check Answer: [27]
8. (a) How many different types of orbitals are found in principal energy level 2? Provide the letter name for these subshells. (b) How many different types of orbitals are found in principal energy level 4? Provide the letter name for these subshells.
   Check Answer: [28]
9. What is the smallest possible *n* value for an *s* orbital? *p* orbital? *d* orbital? *f* orbital?
   Check Answer: [29]
10. Write the maximum number of electrons allowed in the indicated sublevels: *s* sublevel? *p* sublevel? *d* sublevel? *f* sublevel?
    Check Answer: [30]
11. (a) What is the maximum number of electrons that can occupy (a) the first principal energy level? (b) the second principal energy level? (c) the third principal energy level? (d) the fourth principal energy level?
    Check Answer: [31]
12. State the Heisenberg uncertainty principle. Describe briefly what the principle implies.
    Check Answer: [32]
13. Write a set of quantum numbers for each of the electrons with an *n* of 4 in a Se atom.
    Check Answer: [33]

Section 10.5 – Atomic Structures Of The First 20 Elements.

1. 100% pure Canadian maple syrup disguises nutrients in a sweet natural taste. One 30 ml (2 Tablespoons) serving of pure maple syrup contains 35% of the Daily Value of Manganese. It is also a source of calcium and potassium. (Source: Quebec Maple Syrup Producers (QMSP), 2021). Write the complete electron configurations and noble gas configurations for manganese, calcium, and potassium. **Check Answer:** [34]
2. Water and electrolyte balance is important in maintaining homeostasis in the human body. The main electrolytes (ions) in the body that we get from the food we eat and fluids we drink include sodium, calcium, potassium, chloride, and magnesium. (a) Write the complete electron configurations for the following ions: sodium, magnesium, and chloride. (b) What do you notice about these ions? **Check Answer:** [35]

3. Using complete subshell notation (not abbreviations, $1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms: **Check Answer:** [36]
   a. C ($z = 6$)
   b. P ($z = 15$)
   c. V ($z = 23$)
   d. Sb ($z = 51$)
   e. Sm ($z = 62$)
4. Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms: **Check Answer:** [37]
   1. N
   2. Si
   3. Fe
   4. Te
   5. Tb
5. Draw the orbital diagram for the valence shell of each of the following atoms: **Check Answer:** [38]
   a. C
   b. P
   c. V
   d. Sb
6. Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

   Check Answer: [39]
   a. N
   b. Si
   c. Fe
   d. Te
7. Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

   Check Answer: [40]
   a. N^{3-}
   b. Ca^{2+}
   c. S^-
   d. Cs^{2+}
   e. Fe^{3+}
   f. Cd^{2+}
8. Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

   Check Answer: [41]

9. Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$?
   Check Answer: [42]
10. Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a –2 charge has this configuration?
    Check Answer: [43]
11. Which of the following atoms has only two unpaired electrons?
    Check Answer: [44]
    a. Mg
    b. Si
    c. S
    d. Ge
12. Which atom would be expected to have a half-filled *6p* subshell?
    Check Answer: [45]
13. Which atom would be expected to have a half-filled *4s* subshell?
    Check Answer: [46]
14. In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.
    Check Answer: [47]
15. Thallium ($Z = 81$) was used as a poison in the Agatha Christie mystery story "The Pale Horse." Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.
    Check Answer: [48]
16. Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.
    Check Answer: [49]

Section 10.6 – Atomic Properties And Periodic Table Trends

1. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.
   Check Answer: [50]
2. Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.
   Check Answer: [51]
3. Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

Check Answer: [52]

4. Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.
   Check Answer: [53]
5. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb.
   Check Answer: [54]
6. Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si.
   Check Answer: [55]
7. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?
   Check Answer: [56]
8. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?
   Check Answer: [57]
9. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.
   Check Answer: [58]
10. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.
    Check Answer: [59]
11. Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.
    Check Answer: [60]
12. List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.
    Check Answer: [61]
13. Which atom and/or ion is/are isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?
    Check Answer: [62]
14. Which of the following atoms and ions is/are isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?
    Check Answer: [63]
15. Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^-, K^+, Rb^+, Mg^{2+}.
    Check Answer: [64]
16. The ionic radii of the ions S^{2-}, Cl^-, and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.
    Check Answer: [65]
17. Which main group atom would be expected to have the lowest second ionization energy?
    Check Answer: [66]

18. Explain why Al is a member of group 13 rather than group 3.
   Check Answer: [67]

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References

Quebec Maple Syrup Producers (QMSP). (2021, December 27). *Nutritional benefits.* Pure Maple from Canada. Retrieved December 1, 2022, from https://www.puremaplefromcanada.com/nutrition/).

Wikipedia contributors. (2022, February 1). *CKUN-FM.* Wikipedia. https://en.wikipedia.org/wiki/CKUN-FM

Notes

1. The spectrum consists of coloured lines, at least one of which (probably the brightest) is red.
2. Visible light spectrum; $v = 6.7 \text{ x } 10^{14} \text{ s}^{-1}$ or Hz
3. $\lambda = 2.960$ m
4. 3.15 m
5. 4.558×10^{-19} J; Watch "6.4 | A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor" for an explanation of the solution to this question
6. 3.233×10^{-19} J; 2.018 eV; Watch "6.5 | Light with a wavelength of 614.5 nm looks orange" for an explanation of the solution to this question
7. $v = 4.469 \times 10^{14} \text{ s}^{-1}$; $\lambda = 6.708 \times 10^{-7}$ m or 670.8 nm; Total Energy in 1 mole of photons = 1.783×10^5 J/mol or J mol^{-1}; Colour of light = Red; Watch "6.6 | Heated lithium atoms emit photons of light with an energy of 2.961 × 10^−19 J." for an explanation of the solution to this question.
8. $\nu = 4.568 \times 10^{14} \text{ s}^{-1}$; $\lambda = 6.563 \times 10^{-7}$ m or 656.3 nm; Total Energy in 1 mole of photons = $1.823 \times 10^5 \text{ J mol}^{-1}$; Colour of light = red
9. (a) $v = 3.8 \text{ x } 10^{14} \text{ s}^{-1}$ or Hz; (b) $v = 7.1 \times 10^{14} \text{ s}^{-1}$ or Hz; The colour of (a) is red since wavelength is 790 nm; (b) is purple/violet/ deep blue since wavelength is 420 nm; Watch "6.8 | When rubidium ions are heated to a high

temperature" for an explanation of solution to this question.

10. (a) $\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; (b) $\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; The colour of (a) is red since wavelength is 869 nm; (b) is blue since wavelength is 459 nm; Watch "6.9 | The emission spectrum of cesium contains two lines" for an explanation of solution to this question.
11. $E = 9.502 \times 10^{-15}$ J; $\nu = 1.434 \times 10^{19}\ \text{s}^{-1}$ or Hz; Watch "6.11 | One of the radiographic devices used in a dentist's office" for an explanation of solution to this question.
12. Minimum number of photons required = 1.4×10^{5} photons; Watch "6.12 | The eyes of certain reptiles" for an explanation of solution to this question.
13. If use wavelength of 680 nm for Red: $\nu = 4.4 \times 10^{14}\ \text{s}^{-1}$ or Hz and $E = 2.9 \times 10^{-19}$ J. If use wavelength of 520 nm for Green: $\nu = 5.8 \times 10^{14}$ s−1 or Hz and $E = 3.8 \times 10^{-19}$ J. If use wavelength of 440nm for Blue: $\nu = 6.8 \times 10^{14}$ s−1 or Hz and $E = 4.5 \times 10^{-19}$ J. Somewhat different numbers are also possible if you chose different wavelengths for each colour. Watch "6.13 | RGB color television and computer displays" for an explanation of solution to this question.
14. An n of 3 indicates that an electron in the hydrogen atom is in the third energy level, which is further from the nucleus than the first energy level (n=1). The Bohr model uses the theory of electrostatic attraction between the positively charged nucleus and the negatively charge electron in its orbital. The closer an electron is to the nucleus the more closely it is held by the nucleus. The farther an electron is from the nucleus (in higher shells or energy levels), the less the electrostatic attraction of an electron to the nucleus due to the shielding effect; hence, an electron in energy level 3 will be bound less tightly than an electron in energy level 1.
15. Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.
16. $E_n = -2.179 \times 10^{-18}$ J
17.

$$E \quad E_2 - E_5 = 2.179 \times 10^{-18}\left(\frac{1}{n_2^2} - \frac{1}{n_5^2}\right)\ \text{J}$$

18. $2.179 \times 10^{-18}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 4.576 \times 10^{-19}\ \text{J}$ Watch "6.19 | The electron volt (eV) is a

$$\frac{4.576 \times 10^{-19}\ \cancel{\text{J}}}{1.602 \times 10^{-19}\ \cancel{\text{J}}\ \text{eV}^{-1}} = 2.856\ \text{eV}$$

convenient unit of energy" for an explanation of solution to this question.

19. (a) 6 different wavelengths. (b) Lowest energy would be a jump from $n = 4$ to $n = 3$, and the change in energy is -1.06×10^{-19} J ; the highest energy would be a jump from $n = 4$ to $n = 1$, and the change in energy is -2.04×10^{-18} J. Recall that a negative energy value means that energy is being released. (c) For the lowest energy jump ($n = 4$ to $n = 3$), $\nu = 1.60 \times 10^{14}\ \text{s}^{-1}$ and $\lambda = 1.87 \times 10^{-6}$ m, which is indicative of infrared radiation (1870 nm); for the highest energy jump ($n = 4$ to $n = 1$), $\nu = 3.08 \times 10^{15}\ \text{s}^{-1}$ and $\lambda = 9.73 \times 10^{-8}$ m, which is indicative of UV radiation (97.3 nm). Watch "6.28 | Consider a large number of hydrogen atoms with electrons" for an explanation of solution to this question.
20. Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The

orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

21. (a) Every line represents a specific wavelength of discrete energies that is emitted when electrons transition from a higher energy shell to a lower energy shell. The emitted light corresponds to energies of the specific electrons. (b) The colours of the lines are different because different wavelengths equate to different discrete energies that represent a specific colour. (c) The line spectrum of iron is more complicated than hydrogen (which only has four lines). Hydrogen (atomic number = 1) only has 1 electron, where iron (atomic number = 26) has 26 electrons. As a result, iron has more energy shell transition possibilities for its electrons and will have a more complicated emission line spectra than hydrogen.
22. Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, $n = 1, 2, 3, \ldots$, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same spatial extent; the angular momentum quantum number l, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same l (and n) all have the same energy; and the orientation quantum number m, which is a measure of the z component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [*s* orbitals] can have zero angular momentum). (**Answer Source:** Answer to this question was retrieved from Problem 2.3.7 in General Chemistry II (Addie Clark). LibreTexts. licensed under CC BY-NC-SA 3.0)
23. The principal quantum number (n) values are 1, 2, 3, 4, and so on. The angular momentum quantum number *(l)* can be any integer between 0 and n - 1. It specifies the type of subshell, specifically the 3D shape of an orbital (0 = *s*; 1 = *p*; 2 = *d*; 3 = *f*; and so on. If $n = 3$, for example, l can be either 0, 1, or 2. The third energy level can have electrons occupying *s, p* or *d* orbitals. The magnetic quantum number (m_l) can be any integer between $-l$ and $+l$. This number divides the subshell into individual orbitals which hold two electrons per orbital; there are $2l+1$ orbitals in each subshell. If $l = 2$, m_l can be either -2, -1, 0, +1, or +2 (a *d* subshell has 5 orbitals, each can contain 2 electrons). Spin quantum number (m_s) specifies the orientation of the spin axis of an electron. An electron can only spin one of two ways where $m_s = \frac{1}{2}$ (up) or $-\frac{1}{2}$ (down). If two electrons share the same orbital, they must have opposite spins.
24. n determines the general range for the value of energy (principal energy level) and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_l determines the orientation of the orbitals of the same l value with respect to one another; it divides subshell into individual orbitals, which hold two electrons per orbital (there are $2l+1$ orbitals in each subshell). m_s determines the spin of an electron.
25. (a) 2p; (b) 4*d*; (c) 6*s*

26. The orbitals which have the same energy [belong to the same subshell and shell (energy level, *n*)] are called degenerate orbitals. Therefore, 2*p* contains 3 degenerate orbitals; 4*d* contains 5 degenerate orbitals; 6*s* is not degenerate.

27. (a) 3*d;* (b) 1*s* (c) 4*f*

28. The orbitals which have the same energy [belong to the same subshell and shell (energy level, *n*)] are called degenerate orbitals. Therefore, 3*d* contains 5 degenerate orbitals; 1*s* is not degenerate; 4*f* contains 7 degenerate orbitals.

29. n = 2 has two possible subshells *s* and *p*; n = 4 has four possible subshells *s, p, d* and *f.*

30. The smallest possible *n* value for an *s* orbital is 1*s, p* orbital is 2*p*, d orbital is 3*d*, *f* orbital is 4*f*.

31. *s* sublevel electron capacity is 2 electrons; *p* sublevel electron capacity is 6 electrons; *d* sublevel electron capacity is 10 electrons; *f* sublevel electron capacity is 14 electrons

32. Use electron capacity for a given energy level (shell) = $2n^2$ (a) the first principal energy level can fit $2(1)^2 = 2$ electrons; (b) the second principal energy level can fit $2(2)^2 = 8$ electrons; (c) the third principal energy level can fit $2(3)^2 = 18$ electrons; (d) the fourth principal energy level can fit $2(4)^2 = 32$ electrons

33. Heisenberg's uncertainty principle states that for particles exhibiting both particle and wave nature, It is fundamentally impossible to accurately determine both the position and velocity (momentum of a particle at the same time. The more precise our measurement of position is, the less accurate will be our momentum measurement and vice-versa

34.

n	*l*	m_l	*s*
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

NOTE: Selenium (Se) has 34 electrons, 6 of which are valence electrons in the fourth principal energy level. The quantum numbers for these 6 valence electrons are shown in the Table. Two electrons are found in the 4*s* orbital, the other four are found dispersed amongst the three 4*p* orbitals.

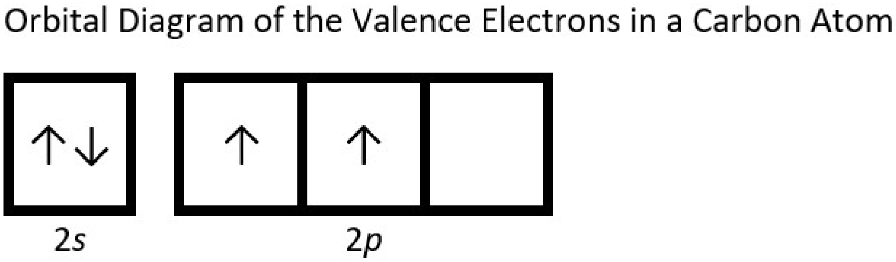
35. manganese - $1s^22s^22p^63s^23p^64s^23d^5$, [Ar]$4s^23d^5$; calcium - $1s^22s^22p^63s^23p^64s^2$, [Ar]$4s^2$; potassium - $1s^22s^22p^63s^23p^64s^1$, [Ar]$4s^1$

36. (a) sodium ion (Na^+) - $1s^22s^22p^6$; magnesium (Mg^{2+}) - $1s^22s^22p^6$; chlorine (Cl^-) - $1s^22s^22p^63s^23p^6$; (b) Both the sodium ion and magnesium ion have the same electron configurations as their closest noble gas, neon (Ne), which all have 10 electrons. A chlorine ion has the same electron configuration as its closest noble gas, argon (Ar), with 18 electrons.

37. (a) C - $1s^22s^22p^2$; P - $1s^22s^22p^63s^23p^3$; V - $1s^22s^22p^63s^23p^64s^23d^3$; Sb - $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^3$; Sm - $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$

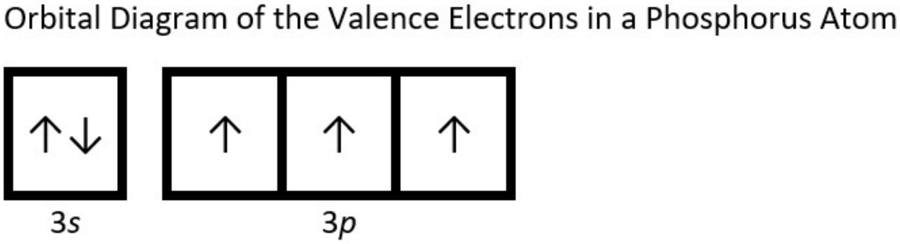
38. (a) $1s^22s^22p^3$; (b) $1s^22s^22p^63s^23p^2$; (c) $1s^22s^22p^63s^23p^64s^23d^6$; (d) $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4$; (e)

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

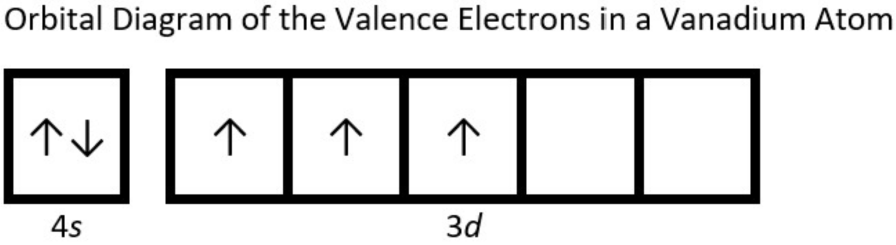


39. (a) C

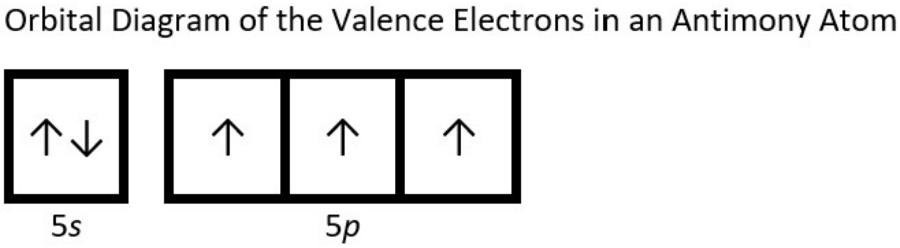
(b) P



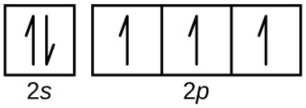
(c) V

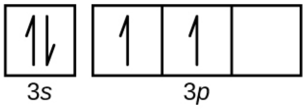


(d) Sb



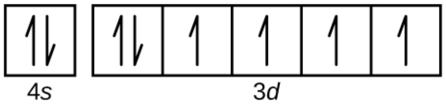
40. (a) N



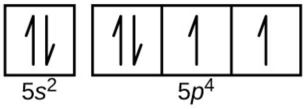


(b) Si

(c) Fe



(d) Te



41. (a) $1s^22s^22p^6$; (b) $1s^22s^22p^63s^23p^6$; (c) $1s^22s^22p^63s^23p^5$; (d) $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^5$; (e) $1s^22s^22p^63s^23p^63d^5$; (f) $1s^22s^22p^63s^23p^64s^23d^{10}4p^64d^{10}$
42. Zr, Zicronium
43. Co, Cobalt
44. Rb^{+1} (Rubidium ion); Se^{2-} (Selenium Ion)
45. answer (b) and (d) are correct. Silicon and Germanium both have only 2 unpaired electrons.
46. Bi, Bismuth
47. K, Potassium
48. Co^{2+} - $1s^22s^22p^63s^23p^63d^7$; Co^{3+} - $1s^22s^22p^63s^23p^63d^6$
49. $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^24f^{14}5d^{10}$
50. Cobalt (Co) has 27 protons, 27 electrons, and 33 neutrons: $1s^22s^22p^63s^23p^64s^23d^7$. Iodine (I) has 53 protons, 53 electrons, and 78 neutrons: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$
51. Cl
52. Rb
53. O
54. Cs
55. Rb < Li < N < F
56. Mg < Si < S < O
57. 15 (5A)
58. 2 (2A) Alkaline Earth Metals
59. Mg < Ca < Rb < Cs
60. Cl < Si < Ca < Sr
61. $Si^{4+} < Al^{3+} < Ca^{2+} < K^+$
62. Li^+, Mg^{2+}, Br^-, Te^{2-}
63. Se, As^- (all have 34 electrons)
64. Cl^{3+}, Si (all have 14 electrons)
65. $Mg^{2+} < K^+ < Rb^+ < Br^- < As^{3-}$
66. Even though all these options have the same number of electrons, they have different numbers of protons, which determines their size. An increase in protons, increases the positive charge inside the nucleus of the atom, which has a greater attraction and pull of those electrons. When comparing atoms with the same number of electrons, the greater the atomic number, the smaller the radius.
67. Ra; Watch "6.85 | Which main group atom would be expected to have the lowest second ionization energy?" for an explanation of the solution to the math portion of this question visit
68. The periodic table is arranged in accordance with increasing atomic number (increasing number of protons and electrons). The groups are arranged according to their chemical behaviours, which is dictated by the number of valence electrons typical for that neutral element. Based on the rules of orbital filling of electrons, aluminum has 13 electrons to fill its orbitals. Al is a p-block element, and electrons must fill 3*p* block before 4*s* or 3*d*. The group 3 elements are *d*-block elements, which are also known as transition elements. This is why Al does not have any properties like *d*-block elements; rather, Al has similar properties of elements found in group 13 (3A).

CHAPTER 11: CHEMICAL BONDING

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The types of bonds that can occur when elements interact
- Application of electron configurations to predict chemical bonding
- Molecular structures and bond strengths

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Periodic Table
- Electron valence configuration of elements

Figure 11a Nicknamed “buckyballs,” buckminsterfullerene molecules (C_{60}) contain only carbon atoms. Here they are shown in a ball-and-stick model (left). These molecules have single and double carbon-carbon bonds arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (centre). This unconventional molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit left: *Chemistry (OpenStax)*, CC BY 4.0; credit middle: modification of work by “Petey21”, CC0; credit right: modification of work by Bill Morrow, CC BY 2.0)

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene, commonly known as a “buckyball.” This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60}, and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.

Watch How atoms bond – George Zaidan and Charles Morton (4 mins)

Indigenous Perspective: Iglu

Igluit are built over the depression from where the blocks are cut. The entryway for the iglu is below ground level. The thermal properties ensures that the inside of the iglu is sufficiently warm even when the temperature outside is very low. (Anderson & Rayner-Canham, para. 11)

“As a result of the unique open crystal structure, snowflakes do not pack well together. This phenomenon results in one of the most important attributes of snow: its thermal insulation properties.” “When the Inuit transitioned from building igluit to using cabins and houses, we used the snow instead to pack tightly against the walls to insulate our homes.”

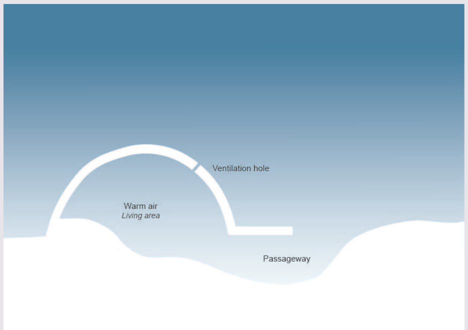


Figure 11.b Cross section of an iglu (credit: graphic by Revathi Mahadevan, CC BY 4.0)

Source: Andersen, C.C., & Rayner-Canham, G. (2019, December). Snow: Making life possible in the Arctic: Chemistry Inuit Life and Culture. *Chem 13 News Magazine*.

Attribution & References

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11.1 IONIC BONDING

Learning Objectives

By the end of this section, you will be able to:

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by **ionic bonds**: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 11.1a). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.

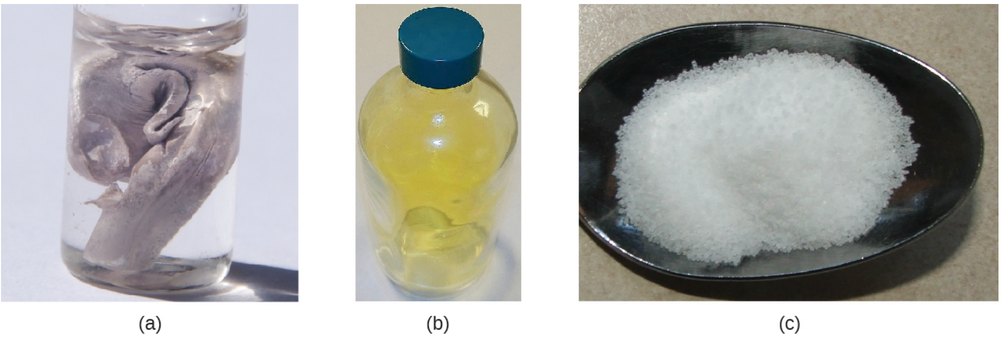

Figure 11.1a (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by Jurii, CC BY 3.0; b: work by Greenhorn1, PD; c: work by Chemicalinterest, PD)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) “molecule” because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure 11.1b).

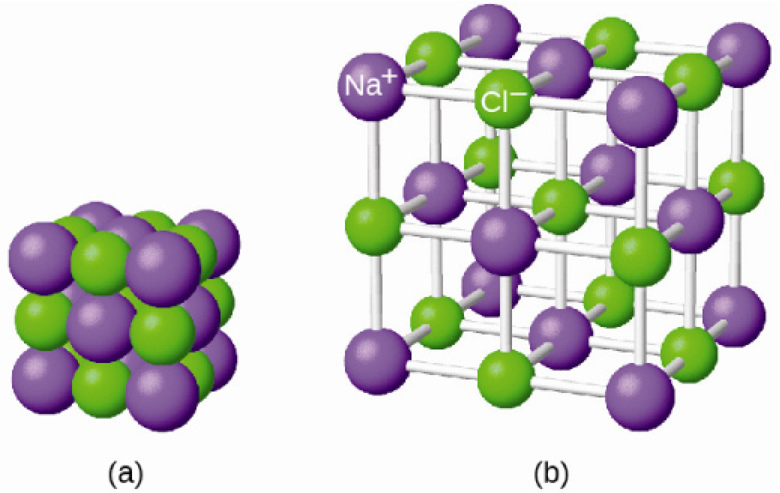

Figure 11.1b The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \qquad \Delta H = 769 \text{ kJ}$$

Similarly, ionic compounds can be formed from polyatomic ions. As in the above example, energy would be required to dissociate the Na^+ and SO_4^{2-} ions of sodium sulfate because of the strong attraction between the ions. When dissociation occurs, any polyatomic ions retain their formula and charge.

$$\mathrm{Na_2SO_4}(s) \longrightarrow 2\mathrm{Na}^+(g) + \mathrm{SO_4^{2-}}(g)$$

Electronic Structures of Simple Cations

When forming a cation, an atom of the main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground-state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behaviour involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^{+}, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the **inert pair effect**, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behaviour: it forms a diatomic ion, $Hg_2{}^{2+}$ (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the 4*s* electron and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the 4*s* electron and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 11.1a

Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

Zn: $[Ar]3d^{10}4s^2$

Cr: $[Ar]3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

Zn^{2+}: $[Ar]3d^{10}$

Cr^{3+}: $[Ar]3d^{3}$

Exercise 11.1a

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Check Your Answer[1]

Electronic Structures of Simple Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^22s^22p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^22s^22p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

Example 11.1b

Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: $[Ar]3d^{10}4s^{2}4p^{6}$

I^{-}: $[Kr]4d^{10}5s^{2}5p^{6}$

Exercise 11.1b

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Check Your Answer[2]

Exercise 11.1c

Check Your Learning Exercise (Text Version)
Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions:

a. P
b. I
c. Mg
d. Cl
e. In
f. Cs
g. O
h. Pb
i. Co

Check Your Answer[3]

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Links to Interactive Learning Tools

Explore Ionic Bonding from the Physics Classroom.

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Notes

1. K^+: [Ar], Mg^{2+}: [Ne]
2. P: $[Ne]3s^2 3p^3$; P^{3-}: $[Ne]3s^2 3p^6$
3. P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

11.2 COVALENT BONDING

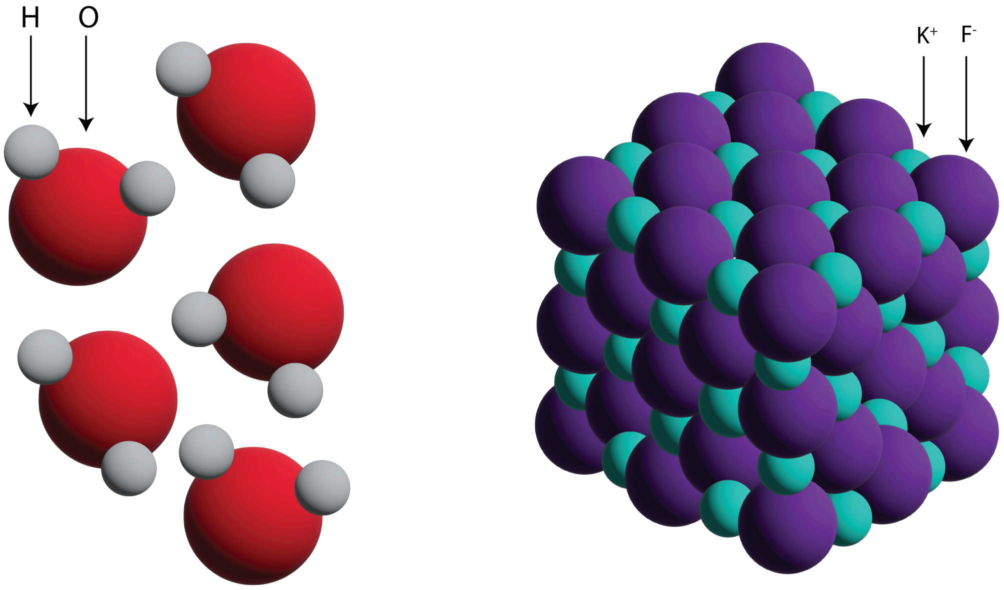
Learning Objectives

By the end of this section, you will be able to:

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons equally between each other. Such bonds are called **covalent bonds**. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.



Water

Potassium fluoride

Figure 11.2a The figure shows the structure of a water molecule and potassium fluoride. (credit: graphic by Revathi Mahadevan, CC BY 4.0.)

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 11.2a illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The **bond length** is determined by the distance at which the lowest potential energy is achieved.

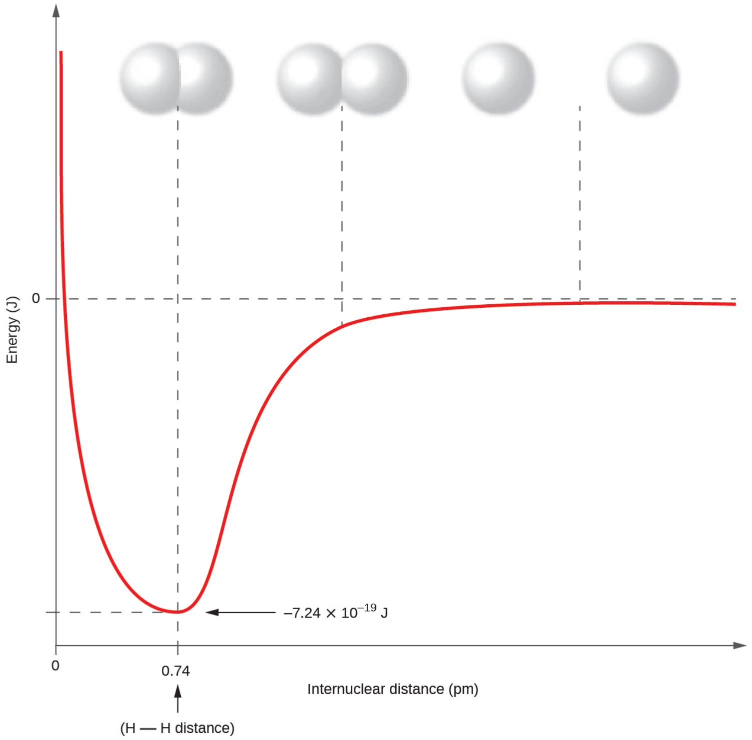


Figure 11.2b The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved (credit: *Chemistry (OpenStax)*, CC BY 4.0).

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2}(g) \longrightarrow 2\mathrm{H}(g) \qquad \Delta H = 436 \text{ kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \qquad \Delta H = -436 \text{ kJ}$$

Exercise 11.2a

Check Your Learning Exercise (Text Version)

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

- a. Cl_2CO
- b. MnO
- c. NCl_3
- d. $CoBr_2$
- e. K_2S
- f. CO

- a. CaF_2
- b. HI
- c. CaO
- d. IBr
- e. CO_2

Check Your Answer[1]

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Non-Polar vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **non-polar covalent bond**. Electrons shared in non-polar (or pure) covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a non-polar covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent**

bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 11.2b shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 11.2a, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 11.2b.

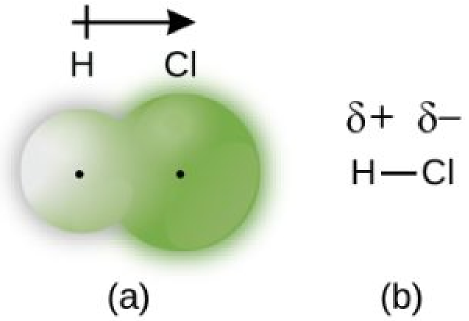

Figure 11.2c (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols **δ**+ and **δ**– indicate the polarity of the H–Cl bond (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 11.2b

Check Your Learning Exercise (Text version)
Why is it incorrect to speak of a molecule of solid NaCl?

Check Your Answer[2]

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Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) toward itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 11.2c shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 11.2d). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

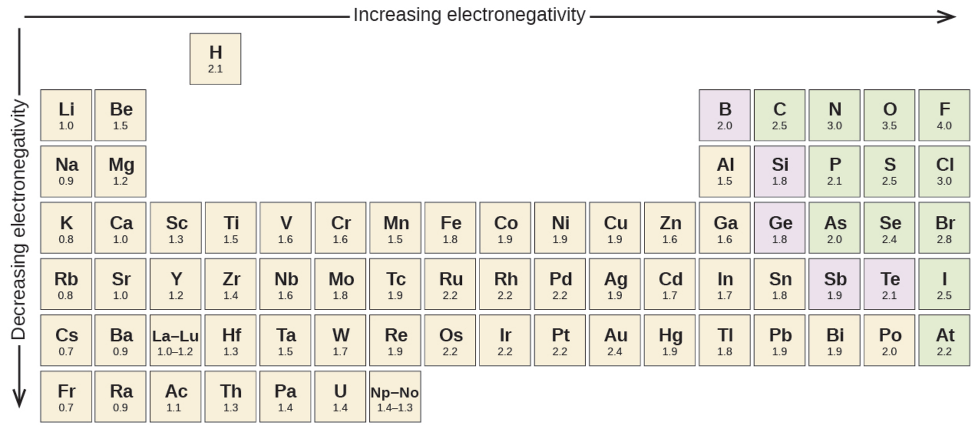


Figure 11.2d The electronegativity values derived by Pauling follow predictable periodic trends with higher electronegativities toward the upper right of the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Linus Pauling

Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

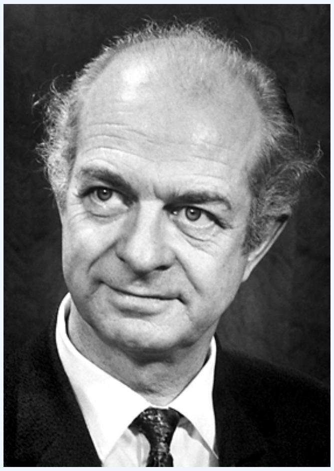


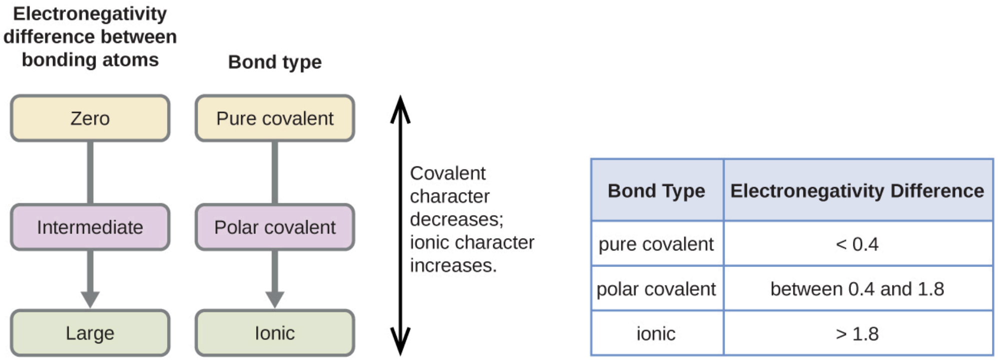
Figure 11.2e Linus Pauling (1901–1994). (credit: work by unknown, courtesy of Nobel Foundation, PD)

Linus Pauling, shown in Figure 11.2e, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent, or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 11.2e shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 11.2f As the electronegativity difference increases between two atoms, the bond becomes more ionic (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 11.2e. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, $NO_3{}^-$, and $NH_4{}^+$, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic $NO_3{}^-$ anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and $NO_3{}^-$, as well as covalent between the nitrogen and oxygen atoms in $NO_3{}^-$.

Example 11.2a

Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 11.2e, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the **δ**– designation is the more electronegative of the two. Table 11.a shows these bonds in order of increasing polarity.

Table 11.2a Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{\mathrm{C}} - \overset{\delta+}{\mathrm{H}}$
S–H	0.4	$\overset{\delta-}{\mathrm{S}} - \overset{\delta+}{\mathrm{H}}$
C–N	0.5	$\overset{\delta+}{\mathrm{C}} - \overset{\delta-}{\mathrm{N}}$
N–H	0.9	$\overset{\delta-}{\mathrm{N}} - \overset{\delta+}{\mathrm{H}}$
C–O	1.0	$\overset{\delta+}{\mathrm{C}} - \overset{\delta-}{\mathrm{O}}$
O–H	1.4	$\overset{\delta-}{\mathrm{O}} - \overset{\delta+}{\mathrm{H}}$

Exercise 11.2c

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 11.2e, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols **δ**+ and **δ**–.

Check Your Answer[3]

Attribution & References

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Notes

1.
    1. ionic: b, d, e, g, i
    2. covalent: a, c, f, h, j, k
2. NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.
3. **Solutions to Exercise 11.2c**

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{\text{C}} - \overset{\delta+}{\text{H}}$
Si–C	0.7	$\overset{\delta+}{\text{Si}} - \overset{\delta-}{\text{C}}$
Si–O	1.7	$\overset{\delta+}{\text{Si}} - \overset{\delta-}{\text{O}}$

11.3 LEWIS SYMBOLS AND STRUCTURES

Learning Objectives

By the end of this section, you will be able to:

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

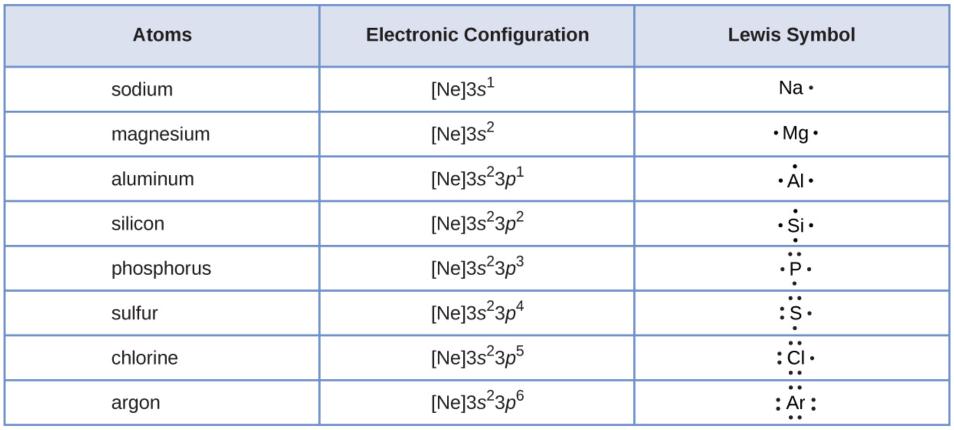
Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons as shown in Figure 11.3a.

Figure 11.3a Lewis structure of calcium atom (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Lewis symbols illustrate the number of valence electrons for each element in the third period of the periodic table as shown in Figure 11.3b. Figure 11.3c shows the Lewis symbols for the first twenty elements of the periodic table.



Atoms	Electronic Configuration	Lewis Symbol
sodium	$[\text{Ne}]3s^1$	$\text{Na}\cdot$
magnesium	$[\text{Ne}]3s^2$	$\cdot\text{Mg}\cdot$
aluminum	$[\text{Ne}]3s^2 3p^1$	$\cdot\overset{\cdot}{\text{Al}}\cdot$
silicon	$[\text{Ne}]3s^2 3p^2$	$\cdot\underset{\cdot}{\overset{\cdot}{\text{Si}}}\cdot$
phosphorus	$[\text{Ne}]3s^2 3p^3$	$\cdot\underset{\cdot}{\overset{\cdot\cdot}{\text{P}}}\cdot$
sulfur	$[\text{Ne}]3s^2 3p^4$	$:\underset{\cdot}{\overset{\cdot\cdot}{\text{S}}}\cdot$
chlorine	$[\text{Ne}]3s^2 3p^5$	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}\cdot$
argon	$[\text{Ne}]3s^2 3p^6$	$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Ar}}}:$

Figure 11.3b Lewis symbols illustrate the number of valence electrons for each element in the third period of the periodic table (credit: *Chemistry (OpenStax)*, CC BY 4.0).

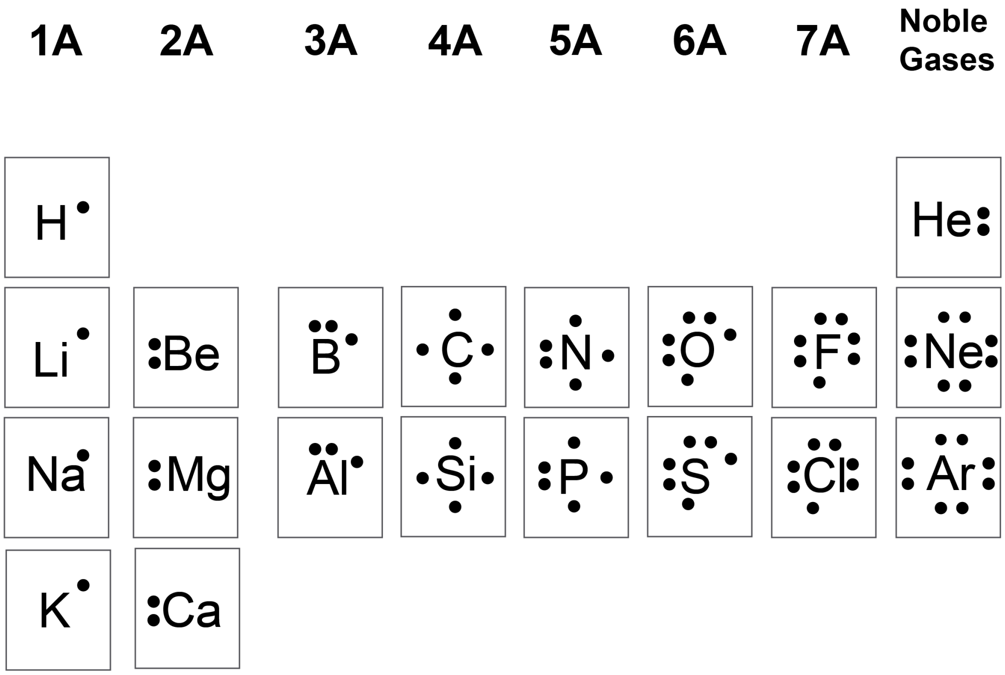


Figure 11.3c Lewis symbols for elements of the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A. (credit: graphic by Revathi Mahadevan, CC BY 4.0)

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:

Figure 11.3d Formation of sodium and calcium cations shown as Lewis structures (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:

Figure 11.3e Formation of chloride and sulfide anions shown as Lewis structures (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Figure 11.3f demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

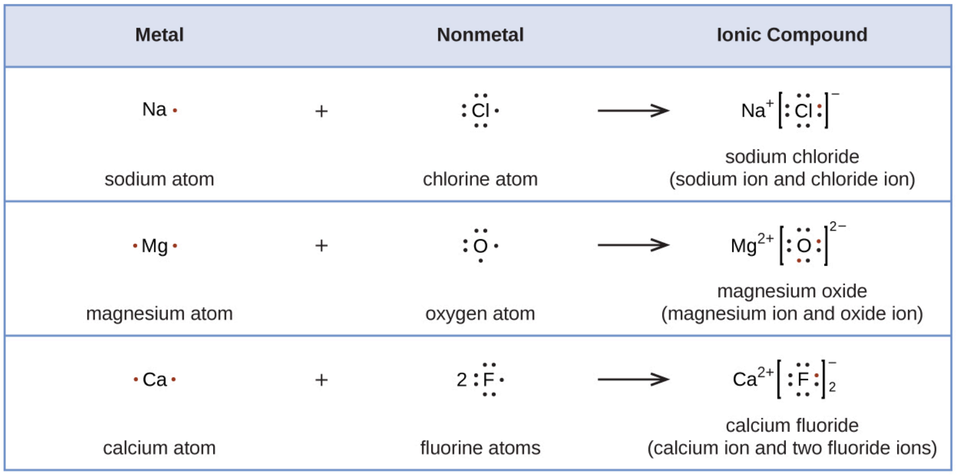


Figure 11.3f Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:

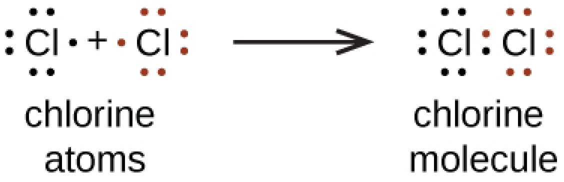


Figure 11.3g Two chlorine atoms bonding for form chlorine diatomic molecule, Cl_2, shown as Lewis structures (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

Figure 11.3h Lewis structure of hydrogen diatomic molecule, H_2, and chlorine diatomic molecule, Cl_2, (with lone pairs) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:

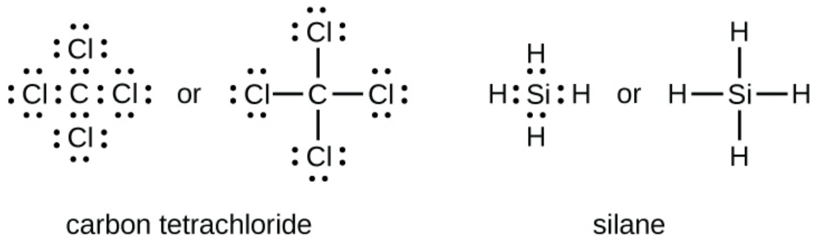


Figure 11.3i Lewis structures of carbon tetrachloride, CCl_4, and silane, SiH_4. Bonding pairs of electrons can be as a bash or bond between atoms (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:

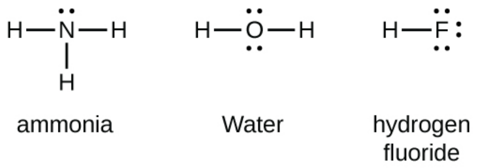


Figure 11.3j Lewis structures of ammonia, NH_3, water, H_2O, and hydrogen fluoride, HF (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

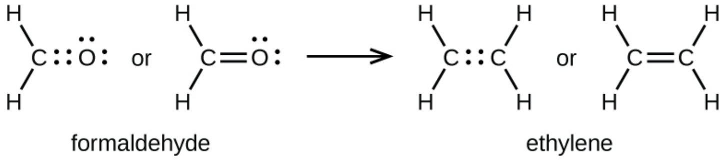


Figure 11.3k Lewis structures of formaldehyde, CH_2O, and ethylene, C_2H_2, showing double bonds (two shared pairs of electrons) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):

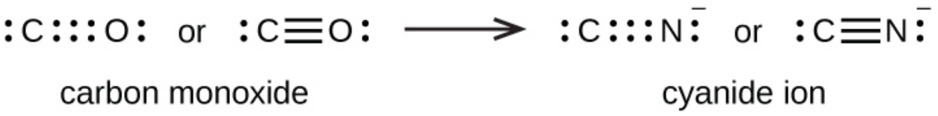


Figure 11.3l Lewis structures of carbon monoxide, CO, and cyanide ion, CN^-, showing triple bonds (three shared pairs of electrons) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:

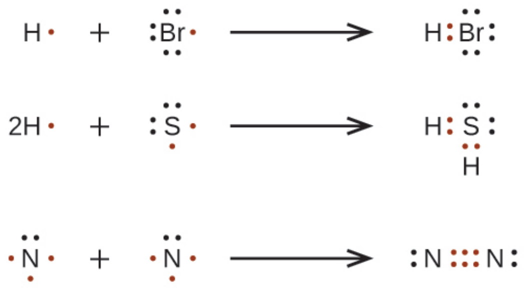


Figure 11.3m Lewis structures of the formation of hydrogen bromide, HBr, hydrogen sulfide, H_2S, and nitrogen, N_2 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the centre.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

   - For a molecule, we add the number of valence electrons on each atom in the molecule:

     $$\begin{array}{r l}
     & \mathrm{SiH_4} \\
     \text{Si: 4 valence electrons/atom} \times 1 \text{ atom} & = 4 \\
     + \quad \text{H: 1 valence electron/atom} \times 4 \text{ atoms} & = 4 \\ \hline
     & = 8 \text{ valence electrons}
     \end{array}$$

   - For a *negative ion*, such as $\mathrm{CHO_2}^-$, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

     $$\begin{array}{r l}
     & \mathrm{CHO_2}^- \\
     \text{C: 4 valence electrons/atom} \times 1 \text{ atom} & = 4 \\
     \text{H: 1 valence electron/atom} \times 1 \text{ atom} & = 1 \\
     \text{O: 6 valence electrons/atom} \times 2 \text{ atoms} & = 12 \\
     + \qquad \text{1 additional electron} & = 1 \\ \hline
     & = 18 \text{ valence electrons}
     \end{array}$$

   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

     $$\begin{array}{r l}
     & \mathrm{NO}^+ \\
     \text{N: 5 valence electrons/atom} \times 1 \text{ atom} & = 5 \\
     \text{O: 6 valence electrons/atom} \times 1 \text{ atom} & = 6 \\
     + \qquad -1 \text{ electron (positive charge)} & = -1 \\ \hline
     & = 10 \text{ valence electrons}
     \end{array}$$

   - Since $\mathrm{OF_2}$ is a neutral molecule, we simply add the number of valence electrons:

     $$\begin{array}{r l}
     & \mathrm{OF_2} \\
     \text{O: 6 valence electrons/atom} \times 1 \text{ atom} & = 6 \\
     + \quad \text{F: 7 valence electrons/atom} \times 2 \text{ atoms} & = 14 \\ \hline
     & = 20 \text{ valence electrons}
     \end{array}$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote

ions with brackets around the structure, indicating the charge outside the brackets:)

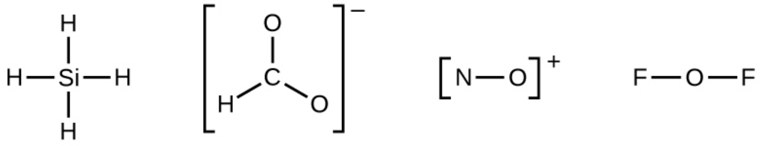


Figure 11.3n Skeletal structures (incomplete Lewis structures) of SiH_4, CHO_2^-, NO^+, and OF_2. Step 2 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

   - There are no remaining electrons on SiH_4, so it is unchanged:

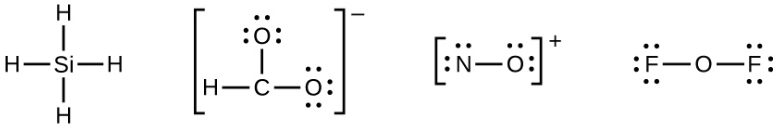


Figure 11.3o Lewis structure of SiH_4. Skeletal structures (incomplete Lewis structures) of CHO_2^-, NO^+, and OF_2. Step 3 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

4. Place all remaining electrons on the central atom.

   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

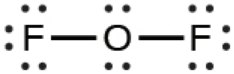


Figure 11.3p Lewis structure of OF_2. Step 4 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
    - SiH_4: Si already has an octet, so nothing needs to be done.
    - CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:

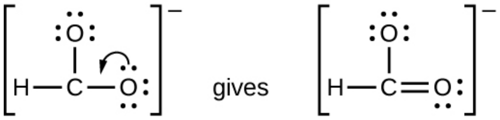


Figure 11.3q Lewis structure of CHO_2^-. Step 5 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

- NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:

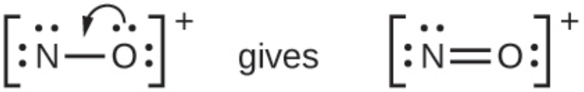


Figure 11.3r Incomplete Lewis structure NO^+. Step 5 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

- This still does not produce an octet, so we must move another pair, forming a triple bond:

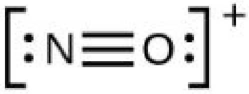


Figure 11.3s Lewis structure of NO^+. Step 5 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

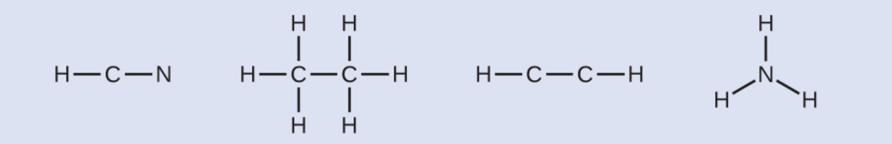
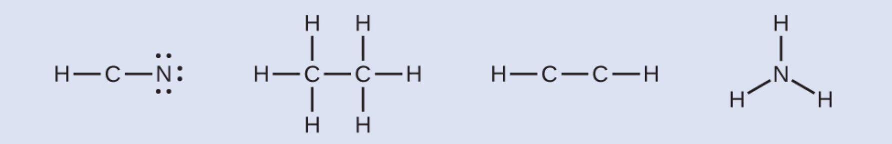
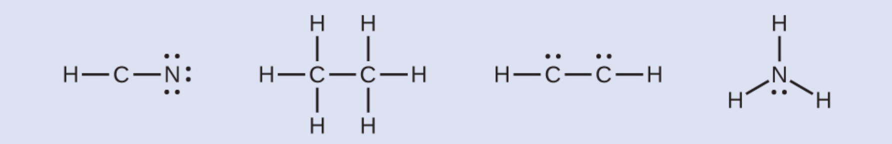
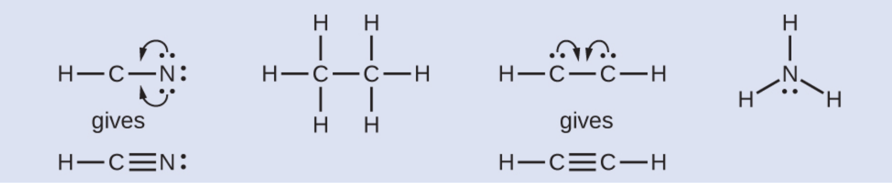
- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 11.3a

Writing Lewis Structures

NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

1. *Calculate the number of valence electrons.*HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10NH_3: (5 × 1) + (3 × 1) = 8
2. *Draw a skeleton and connect the atoms with single bonds.* Remember that H is never a central atom: 
3. *Where needed, distribute electrons to the terminal atoms:*  HCN: six electrons placed on NH_3CCH_3: no electrons remain. HCCH: no terminal atoms capable of accepting electrons. NH_3: no terminal atoms capable of accepting electrons.
4. *Where needed, place remaining electrons on the central atom:*  HCN: no electrons remain. H_3CCH_3: no electrons remain. HCCH: four electrons placed on carbon. NH_3: two electrons placed on nitrogen.
5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*  HCN: form two more C–N bonds. H_3CCH_3: all atoms have the correct number of electrons. HCCH: form a triple

bond between the two carbon atoms. NH_3: all atoms have the correct number of electrons.

Exercise 11.3a

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Check Your Answer[1]

Fullerene Chemistry

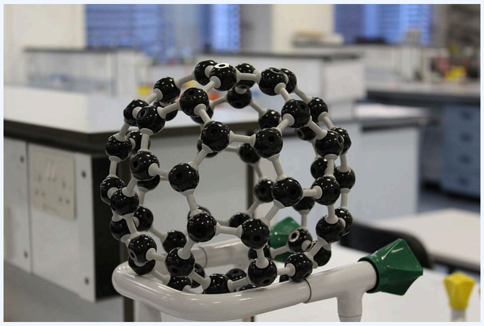


Figure 11.3t This model shows the arrangement of carbon atoms in a fullerene (or 'buckyball') a large molecule made up of 60 carbon atoms. (credit: work by UCL Mathematical and Physical Science, CC BY 2.0)

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 11.3t), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule (Figure 11.a in Chapter 11 Introduction). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honoured him as the "Father of Nanotechnology."

Learn more about Dr. Smalley by reading the article Richard E. Smalley – Facts [New Tab] on the Nobel Prize website.

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

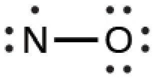


Figure 11.3u Lewis structure of NO where oxygen has been assigned the eight electrons as it is more electronegative compared to nitrogen (credit: *Chemistry (OpenStax)*, CC BY 4.0).

4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

Figure 11.3v The Lewis structure of NO double bond where the electrons are rearranged to obtain octets where a double bond is formed so that nitrogen can move closer to an octet (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 12, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.

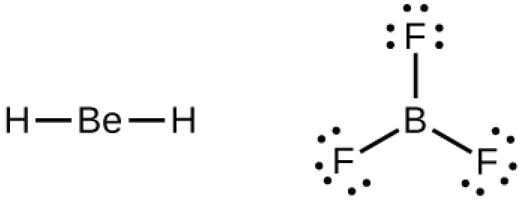


Figure 11.3w The Lewis structures for beryllium dihydride, BeH_2 (left), and boron trifluoride, BF_3 (right) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom (Figure 11.3v).

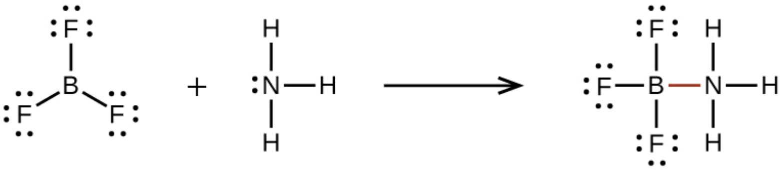


Figure 11.3x The reaction between BF_3 and NH_3 come together to form a single bond between boron and nitrogen because boron requires the lone pair of electrons from nitrogen to fulfill its octet (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules**. Figure 11.3w shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

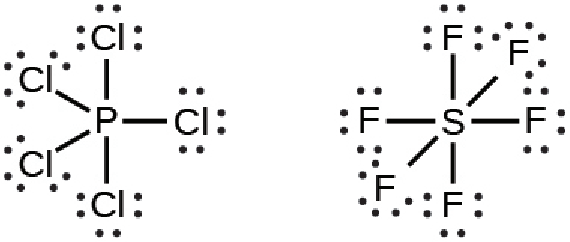


Figure 11.3y The Lewis structures for two hypervalent molecules, PCl_5 and SF_6 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs (Figure 11.3x).

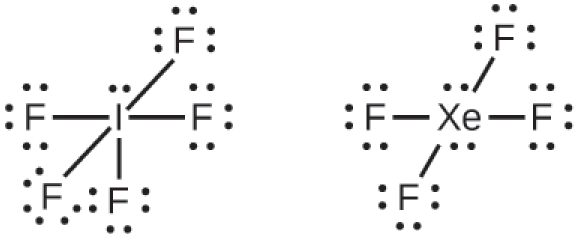


Figure 11.3z The Lewis structures for hypervalent molecules, IF_5 and XeF_4 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

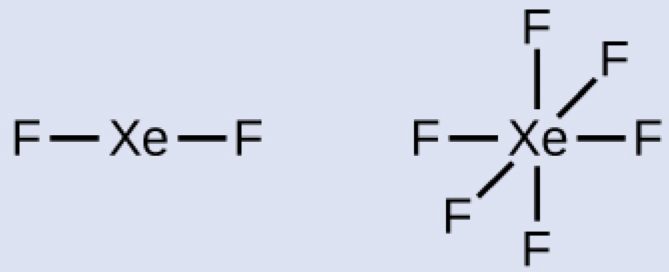
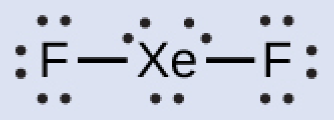
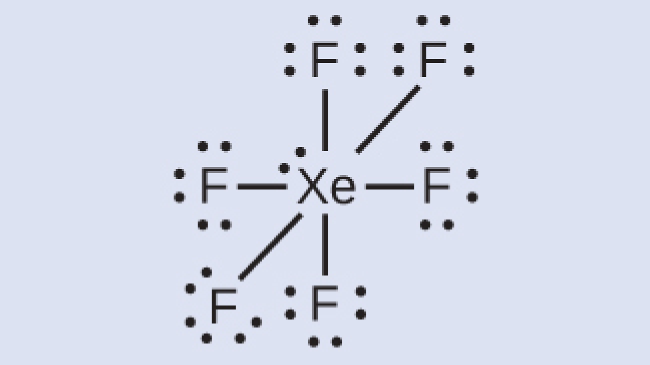
Example 11.3b

Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

1. *Calculate the number of valence electrons:*XeF_2: 8 + (2 × 7) = 22XeF_6: 8 + (6 × 7) = 50
2. *Draw a skeleton joining the atoms by single bonds.* Xenon will be the central atom because fluorine cannot be a central atom:

3. *Distribute the remaining electrons.*XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:

XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:


Exercise 11.3b

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Check Your Answer[2]

Scientists in Action: Dr. Mario J. Molina

Dr. Mario J. Molina is a Mexican chemist who is best known for his role in the discovery of the impact that CFC's (chlorofluorocarbons) have on the ozone layer. He was a co-recipient of the Nobel Prize in Chemistry in 1995.

Figure 11.3aa Dr. Mario J. Molina (credit: work by http://science.in2pic.com, CC BY-SA 3.0)

Part of his work included the hypothesis that CFCs in the upper atmosphere could produce a chlorine radical that would catalyze the destruction of ozone.

$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$

$ClO\cdot + O\cdot \rightarrow Cl\cdot + O_2$

After data was collected that confirmed this hypothesis, steps were taken by countries across the world to discontinue the use of ozone-damaging compounds. The most significant actions were included in the Montreal Protocol [New Tab].

Dr. Molina is currently a faculty member at UC San Diego and is involved in science outreach.

Watch Dr. Molina address students about his inspiration to become a scientist in this Nobel Prize video on YouTube [New Tab].

Links to Interactive Learning Tools

Explore Lewis Electron Dot Structures from the Physics Classroom.

Attribution & References

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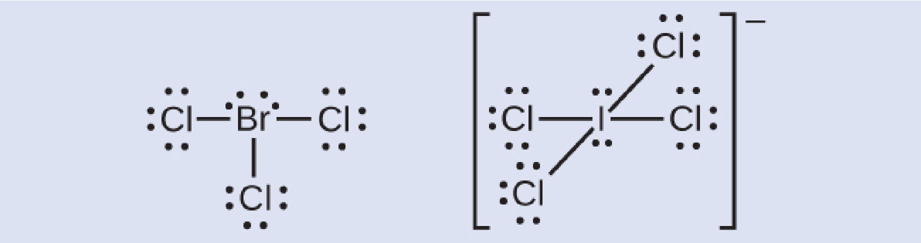
Notes

1. 
2. 

11.4 FORMAL CHARGES AND RESONANCE

Learning Objectives

By the end of this section, you will be able to:

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The **formal charge** of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge} = \#\ \text{valence shell electrons (free atom)}\ -\ \#\ \text{lone pair electrons}\ -\frac{1}{2}\#\ \text{bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

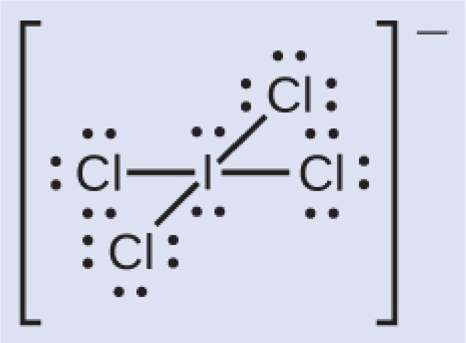
Example 11.4a

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^-.

Solution

1. *We divide the bonding electron pairs equally for all I–Cl bonds:*



2. *We assign lone pairs of electrons to their atoms.* Each Cl atom now has seven electrons assigned to it, and the I atom has eight.
3. *Subtract this number from the number of valence electrons for the neutral atom:* I: 7 – 8 = –1 Cl: 7 – 7 = 0 The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Exercise 11.4a

Calculate the formal charge for each atom in the carbon monoxide molecule:

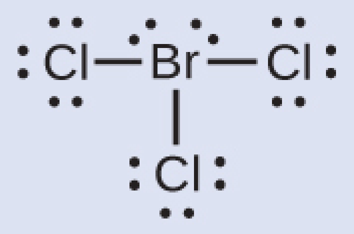
Check Your Answer[1]

Example 11.4b

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*


2. *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons and the Br atom has seven electrons.
3. *Subtract this number from the number of valence electrons for the neutral atom.* This gives the formal charge: Br: 7 – 7 = 0 Cl: 7 – 7 = 0 All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 11.4b

Determine the formal charge for each atom in NCl_3.

Check Your Answer[2]

Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds (Figure 11.4a).

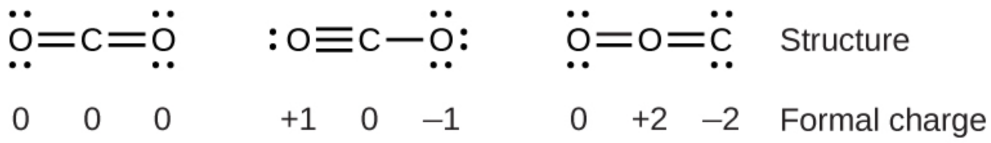


Figure 11.4a Three possible structures for carbon dioxide, CO_2 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^-, NCS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown in Figure 11.4b.

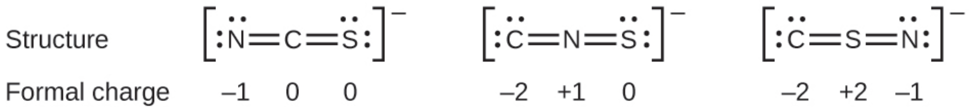


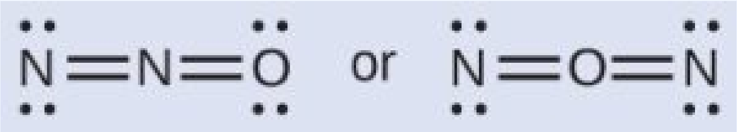
Figure 11.4b Three possible structures for the thiocyanate ion (credit: *Chemistry (OpenStax)*,CC BY 4.0).

Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example 11.4c

Using Formal Charge to Determine Molecular Structure

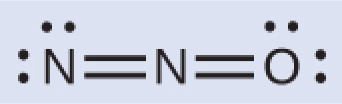
Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution

Determining formal charge yields the following:

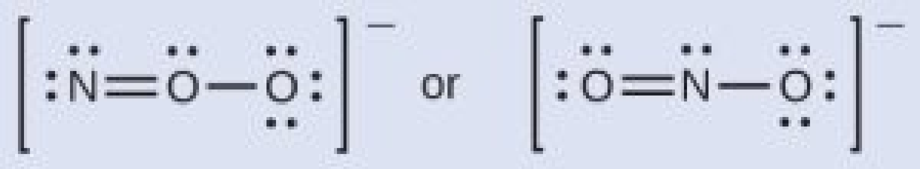
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

Exercise 11.4c

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Check Your Answer[3]

Resonance

You may have noticed that the nitrite anion in Example 3 above can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions as demonstrated in Figure 11.4c.

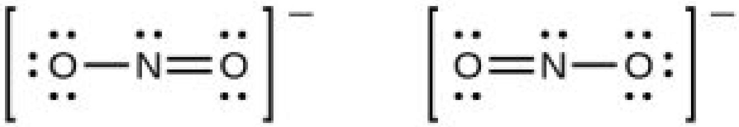


Figure 11.4c The molecular structures for the nitrite anion, NO_2^- (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown in Figure 11.4d.

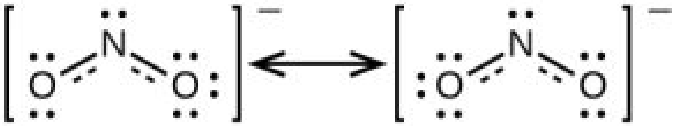


Figure 11.4d The resonance structures of the nitrite anion, NO_2^- (credit: *Chemistry (OpenStax)*, CC BY 4.0).

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-}, provides a second example of resonance as shown in Figure 11.4e.

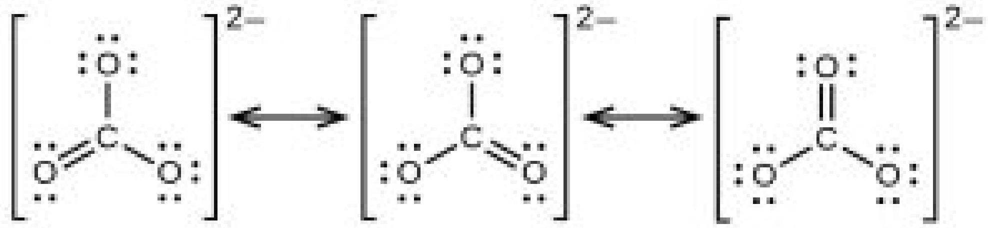


Figure 11.4e The resonance structures for the carbonate anion, CO_3^{2-} (credit: *Chemistry (OpenStax)*, CC BY 4.0).

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Key Equations

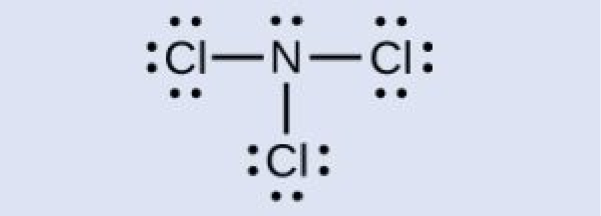
- $\text{formal charge} = \#\ \text{valence shell electrons (free atom)}\ -\ \#\ \text{lone pair electrons}\ -\frac{1}{2}\#\ \text{bonding electrons}$

Attribution & References

Except where otherwise noted, this page is adapted JR van Haarlem from "4.5 Formal Charges and Resonance" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*

Notes

1. C −1, O +1
2. N: 0; all three Cl atoms: 0



3. ONO^-

11.5 STRENGTHS OF IONIC AND COVALENT BONDS

Learning Objectives

By the end of this section, you will be able to:

- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of the reaction

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy (see Figure 11.2b in Chapter 11.2 Covalent Bonding). The stronger a bond, the greater the energy required to break it.

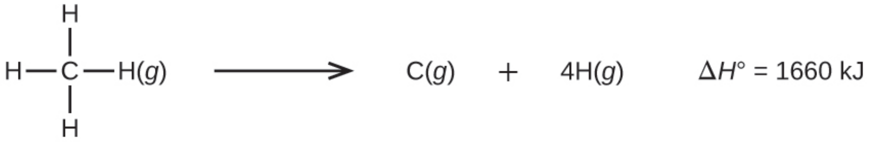
The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, $\text{D}_{\text{X}-\text{Y}}$, is defined as the standard enthalpy change for the endothermic reaction:

$$\text{XY}(g) \longrightarrow \text{X}(g) + \text{Y}(g) \qquad \text{D}_{\text{X}-\text{Y}} = \Delta H^\circ$$

For example, the bond energy of the (non-polar) covalent H–H bond, $\text{D}_{\text{H}-\text{H}}$, is 436 kJ per mole of H–H bonds broken:

$$H_2(g) \longrightarrow 2H(g) \qquad D_{H-H} = \Delta H^\circ = 436 \text{ kJ}$$

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH_4, 1660 kJ, is equal to the standard enthalpy change of the reaction:



The average C–H bond energy, $D_{C–H}$, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 11.5a, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 11.5b. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table 11.5a Bond Energies (kJ/mol)

Bond	Type of Bond	Bond Energy
H–H	single	436
H–C	single	415
H–N	single	390
H–O	single	464
H–F	single	569
H–Si	single	395
H–P	single	320
H–S	single	340
H–Cl	single	432
H–Br	single	370
H–I	single	295
C–C	single	345
C=C	double	611
C≡C	triple	837
C–N	single	290
C=N	double	615
C≡N	triple	891
C–O	single	350
C=O	double	741
C≡O	triple	1080
C–F	single	439
C–Si	single	360
C–P	single	265
C–S	single	260
C–Cl	single	330
C–Br	single	275
C–I	single	240
N–N	single	160
N=N	double	418

N≡N	triple	946
N–O	single	200
N–F	single	270
N–P	single	210
N–Cl	single	200
N–Br	single	245
O–O	single	140
O=O	double	498
O–F	single	160
O–Si	single	370
O–P	single	350
O–Cl	single	205
O–I	single	200
F–F	single	160
F–Si	single	540
F–P	single	489
F–S	single	285
F–Cl	single	255
F–Br	single	235
Si–Si	single	230
Si–P	single	215
Si–S	single	225
Si–Cl	single	359
Si–Br	single	290
Si–I	single	215
P–P	single	215
P–S	single	230
P–Cl	single	330
P–Br	single	270
P–I	single	215
S–S	single	215

S–Cl	single	250
S–Br	single	215
Cl–Cl	single	243
Cl–Br	single	220
Cl–I	single	210
Br–Br	single	190
Br–I	single	180
I–I	single	150

Table 11.5b Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond type	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	single	1.54	345
C=C	double	1.34	611
C≡C	triple	1.20	837
C–N	single	1.43	290
C=N	double	1.38	615
C≡N	triple	1.16	891
C–O	single	1.43	350
C=O	double	1.23	741
C≡O	triple	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic. An exothermic reaction (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, ΔH, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy “in”, positive sign) plus the energy released when all bonds are formed in the products (energy “out,” negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum \mathrm{D}_{\text{bonds broken}} - \sum \mathrm{D}_{\text{bonds formed}}$$

In this expression, the symbol Σ means “the sum of” and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table (like Table 11.5b) and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{2HCl}(g)$$

or

$$\mathrm{H - H}(g) + \mathrm{Cl - Cl}(g) \longrightarrow \mathrm{2H - Cl}(g)$$

To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2 × 432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned}\Delta H = &\quad \sum \mathrm{D_{bonds\ broken}} - \sum \mathrm{D_{bonds\ formed}} \\ \Delta H = &\quad [\mathrm{D_{H-H}} + \mathrm{D_{Cl-Cl}}] - \mathrm{2D_{H-Cl}} \\ = &\quad [436 + 243] - 2(432) = -185\ \mathrm{kJ}\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Appendix H gives a value for the standard molar enthalpy of formation of HCl(g), $\Delta H_\mathrm{f}^\circ$, of –92.307 kJ/mol. Twice that value is –184.6 kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

Example 11.5a

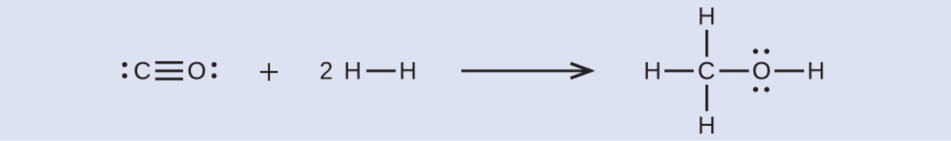
Using Bond Energies to Calculate Approximate Enthalpy Changes

Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table 11.5b, calculate the approximate enthalpy change, Δ*H*, for the reaction here:

$$\mathrm{CO}(g) + \mathrm{2H_2}(g) \longrightarrow \mathrm{CH_3OH}(g)$$

Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\Delta H = \sum \mathrm{D}_{\text{bonds broken}} - \sum \mathrm{D}_{\text{bonds formed}}$$

$$\Delta H = [\mathrm{D}_{\mathrm{C{\equiv}O}} + 2(\mathrm{D}_{\mathrm{H-H}})] - [3(\mathrm{D}_{\mathrm{C-H}}) + \mathrm{D}_{\mathrm{C-O}} + \mathrm{D}_{\mathrm{O-H}}]$$

Using the bond energy values in Table 11.5b, we obtain:

$$\begin{aligned}\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107\ \text{kJ}\end{aligned}$$

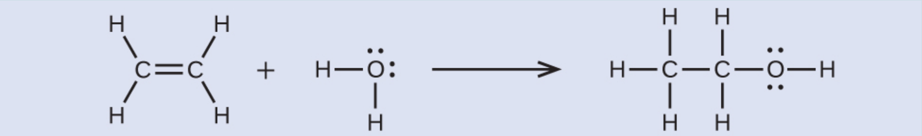
We can compare this value to the value calculated based on $\Delta H_{\mathrm{f}}^{\circ}$ data from Appendix H:

$$\begin{aligned}\Delta H &= [\Delta H_{\mathrm{f}}^{\circ}\mathrm{CH_3OH}(g)] - [\Delta H_{\mathrm{f}}^{\circ}\mathrm{CO}(g) + 2 \times \Delta H_{\mathrm{f}}^{\circ}\mathrm{H_2}] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5\ \text{kJ}\end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

Exercise 11.5a

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



Using the bond energies in Table 11.5b, calculate an approximate enthalpy change, Δ*H*, for this reaction.

Check Your Answer[1]

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy ($\Delta H_{\text{lattice}}$)** of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$\text{MX}(s) \longrightarrow \text{M}^{n+}(g) + X^{n-}(g) \qquad \Delta H_{\text{lattice}}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}} = 769\ \text{kJ}$. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{\text{lattice}}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{\text{C}(\text{Z}^+)(\text{Z}^-)}{\text{R}_0}$$

in which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and R_o is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease.

When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and $Z^- = 1$) is 1023 kJ/mol, whereas that of MgO (Z^+ and $Z^- = 2$) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 11.5b

Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

Exercise 11.5b

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Check Your Answer[2]

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The **Born-Haber cycle** is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- $\Delta H_{\text{f}}^{\circ}$, the standard enthalpy of formation of the compound
- *IE*, the ionization energy of the metal
- *EA*, the electron affinity of the nonmetal
- $\Delta H_{\text{s}}^{\circ}$, the enthalpy of sublimation of the metal
- *D*, the bond dissociation energy of the nonmetal
- $\Delta H_{\text{lattice}}$, the lattice energy of the compound

Figure 11.5a diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

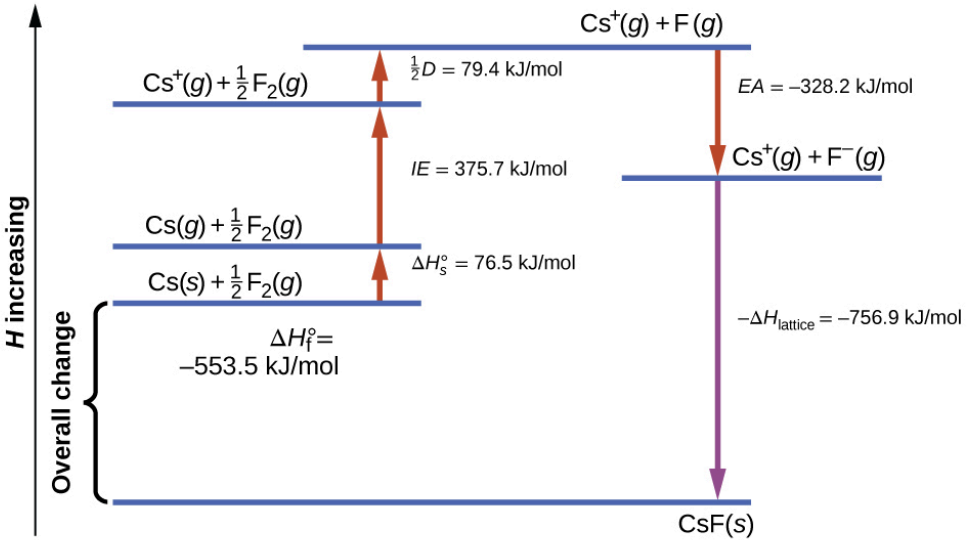


Figure 11.5a The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states (credit: *Chemistry (OpenStax)*,CC BY 4.0).

We begin with the elements in their most common states, Cs(*s*) and F_2(*g*). The $\Delta H_{\text{s}}^{\circ}$ represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the *y*-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, $\Delta H_{\text{f}}^{\circ}$, of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 11.5c shows this for cesium chloride, $CsCl_2$.

Table 11.5c Enthalpies and enthalpy formation for Cesium chloride, $CsCl_2$

Steps in Formation Process	Enthalpy Equations
Enthalpy of sublimation of Cs(*s*)	$\mathrm{Cs}(s) \longrightarrow \mathrm{Cs}(g) \quad \Delta H = \Delta H_s^\circ = 76.5\mathrm{kJ}$
One-half of the bond energy of Cl_2	$\frac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{Cl}(g) \quad \Delta H = \frac{1}{2}\ D = 122\mathrm{kJ}$
Ionization energy of Na(*g*)	$\mathrm{Na}(g) \longrightarrow \mathrm{Na}^+(g) + \mathrm{e}^- \quad \Delta H = IE = 496\mathrm{kJ}$
Negative of the electron affinity of Cl	$\mathrm{Cl}(g) + \mathrm{e}^- \longrightarrow \mathrm{Cl}^-(g) \quad \Delta H = -EA = -368\mathrm{kJ}$
Negative of the lattice energy of NaCl(*s*)	$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \longrightarrow \mathrm{NaCl}(s) \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of NaCl(*s*), add steps 1–5	$\Delta H = \Delta H_\mathrm{f}^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\mathrm{Na}(s) + \frac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{NaCl}(s) = -411\ \mathrm{kJ}$

Thus, the lattice energy can be calculated from other values. For cesium chloride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = (411 + 109 + 122 + 496 + 368)\ \mathrm{kJ} = 770\ \mathrm{kJ}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_s°, ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_{\text{lattice}}$, and standard enthalpy of formation $\Delta H_\mathrm{f}^\circ$ are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much higher than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extensive lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

Key Equations

- Bond energy for a diatomic molecule: $\mathrm{XY}(g) \longrightarrow \mathrm{X}(g) + \mathrm{Y}(g) \quad \mathrm{D}_{\mathrm{X-Y}} = \Delta H^\circ$
- Enthalpy change: $\Delta H = \sum \mathrm{D}_{\text{bonds broken}} - \sum \mathrm{D}_{\text{bonds formed}}$
- Lattice energy for a solid MX: $\mathrm{MX}(s) \longrightarrow \mathrm{M}^{n+}(g) + \mathrm{X}^{n-}(g) \quad \Delta H_{\text{lattice}}$

- Lattice energy for an ionic crystal: $\Delta H_{\text{lattice}} = \frac{\mathrm{C(Z^{+})(Z^{-})}}{\mathrm{R_0}}$

Attribution & References

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Notes

1. −35 kJ
2. ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

11.6 MOLECULAR STRUCTURE AND POLARITY

Learning Objectives

By the end of this section, you will be able to:

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, the molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 11.6a). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

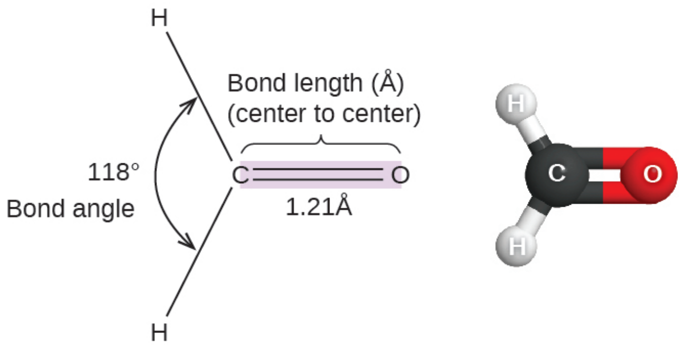


Figure 11.6a Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO (credit: *Chemistry (OpenStax)*,CC BY 4.0).

VSEPR Theory

Watch [What is the shape of a molecule? (3:47 min)]

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 11.6b) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 11.6b).

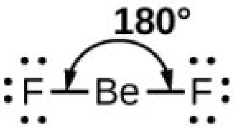


Figure 11.6b The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Figure 11.6c illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a **linear** geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.

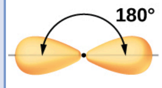
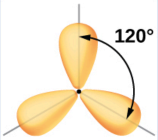
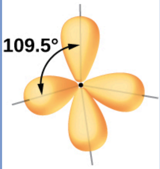
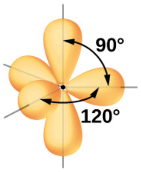
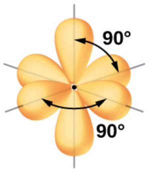
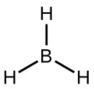
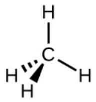
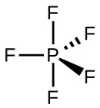
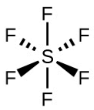
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	H—Be—H				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 11.6c The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs) (credit: *Chemistry (OpenStax)*,CC BY 4.0).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 11.6c describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 11.6d). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 11.6e).

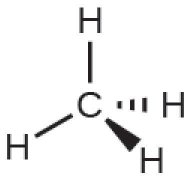


Figure 11.6d Tetrahedral structure of methane, CH_4 (credit: *Chemistry (OpenStax)*,CC BY 4.0).

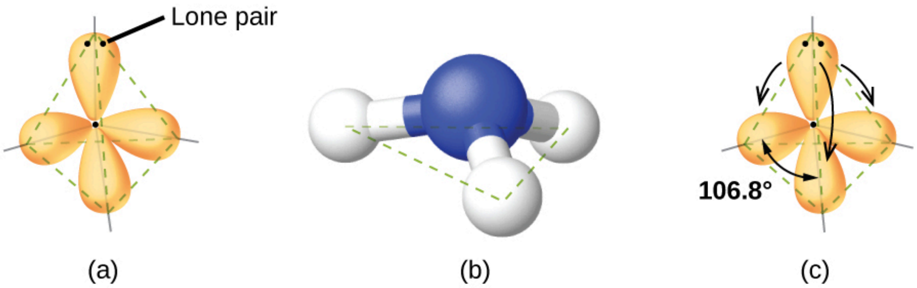


Figure 11.6e (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5° (credit: *Chemistry (OpenStax)*,CC BY 4.0).

As seen in Figure 11.6e, small distortions from the ideal angles in Figure 11.6c can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

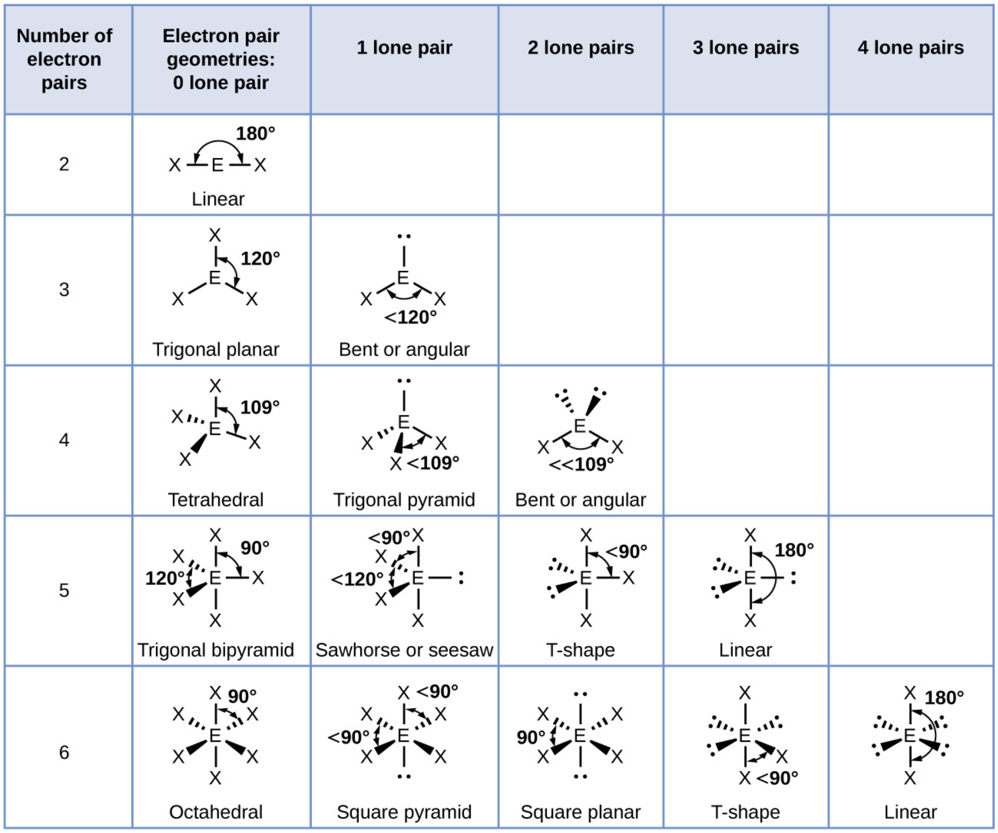
$$\text{lone pair-lone pair} > \text{lone pair-bonding pair} > \text{bonding pair-bonding pair}$$

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

$$\text{lone pair} > \text{triple bond} > \text{double bond} > \text{single bond}$$

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure 11.6a). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 11.6e) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 11.6c) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 11.6e). Figure 11.6f illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.



Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal planar	<120° Bent or angular			
4	109° Tetrahedral	<109° Trigonal pyramid	<<109° Bent or angular		
5	90° 120° Trigonal bipyramid	<90° <120° Sawhorse or seesaw	<90° T-shape	180° Linear	
6	90° Octahedral	<90° <90° Square pyramid	90° Square planar	<90° T-shape	180° Linear

Figure 11.6f The molecular structures are identical to the electron-pair geometries when there is no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry (credit: *Chemistry (OpenStax)*,CC BY 4.0).

According to VSEPR theory, the terminal atom locations (Xs in Figure 11.6f) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 11.6g: an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in Figure 11.6f, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 11.6g). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

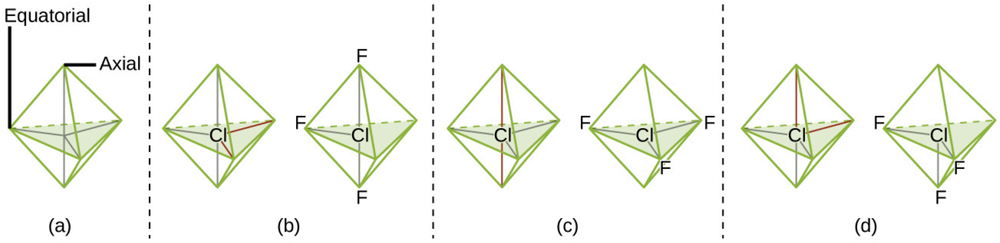


Figure 11.6g (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 11.6f).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 11.6f, first column).

4. Use the number of lone pairs to determine the molecular structure (Figure 11.6f). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

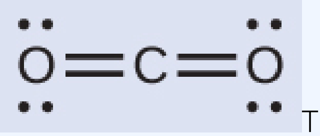
Example 11.6a

Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

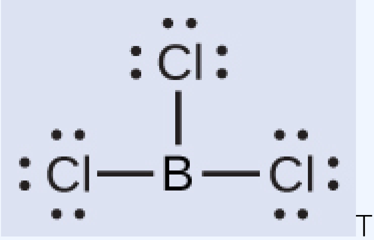
Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

Solution



a. We write the Lewis structure of CO_2 as: This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.



b. We write the Lewis structure of BCl_3 as: Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure (Figure 11.6h).

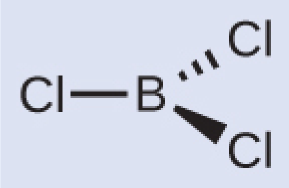


Figure 11.6h Trigonal planar molecule BCl_3

The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Exercise 11.6a

Carbonate, CO_3^{2-}, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Check Your Answer[1]

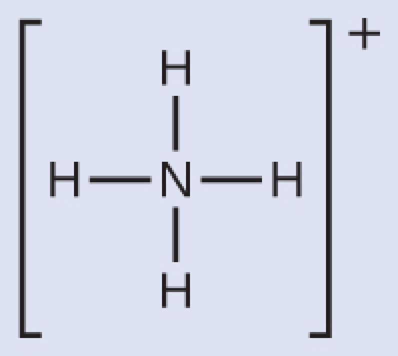
Example 11.6b

Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 11.6i). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral (Figure 11.6i).

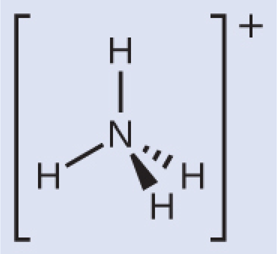


Figure 11.6i The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Exercise 11.6b

Identify a molecule with a trigonal bipyramidal molecular structure.

Check Your Answer[2]

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

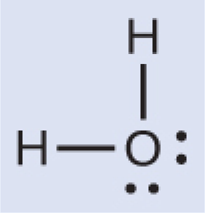
Example 11.6c

Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (Figure 11.6j), as indicated in Figure 11.6e. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

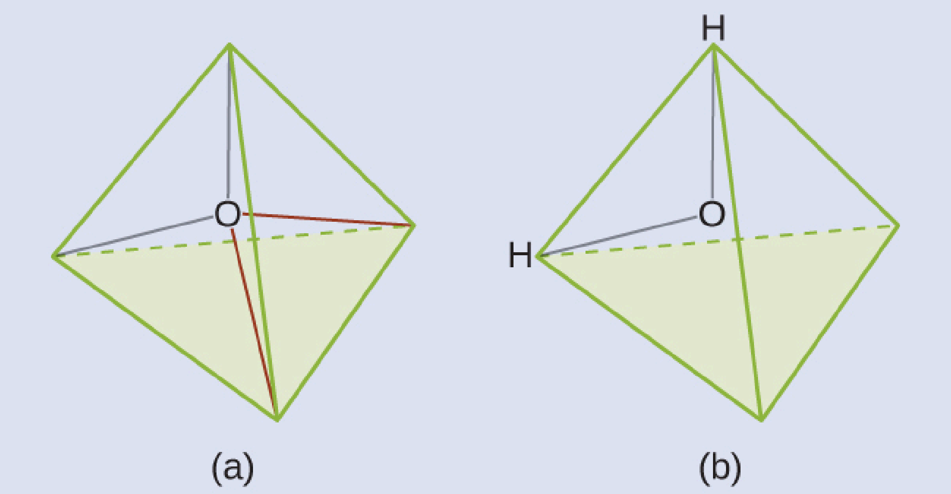


Figure 11.6j (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent (credit: *Chemistry (OpenStax)*,CC BY 4.0).

Exercise 11.6c

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Check Your Answer[3]

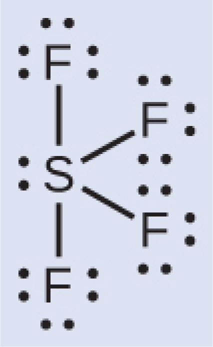
Example 11.6d

Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of an SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure 11.6k) is that of a seesaw (Figure 11.6k).

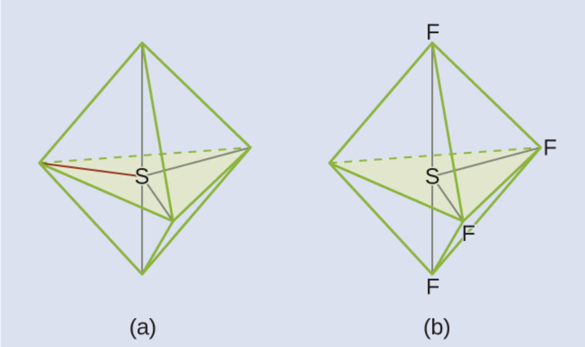


Figure 11.6k (a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 11.6d

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Check Your Answer[4]

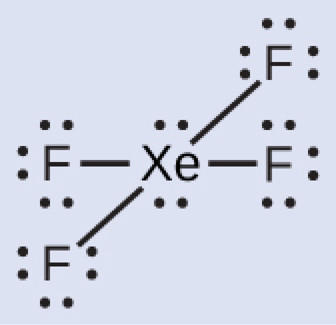
Example 11.6e

Predicting Electron-pair Geometry and Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (Figure 11.6l), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 11.6l). The five atoms are all in the same plane and have a square planar molecular structure.

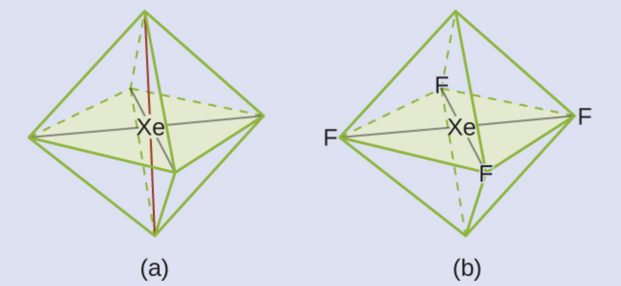


Figure 11.6l (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 11.6e

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Check Your Answer[5]

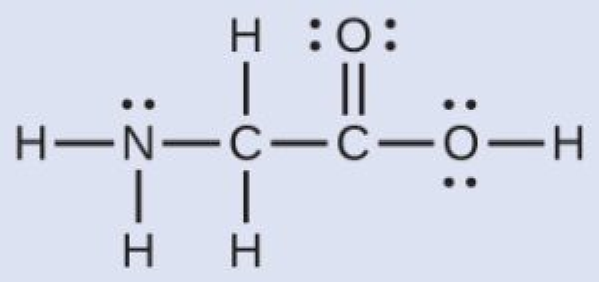
Molecular Structure for Multicentre Molecules

When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

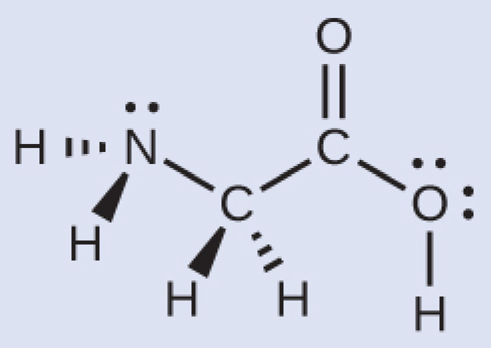
Example 11.6f

Predicting Structure in Multicentre Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

- nitrogen — four regions of electron density; tetrahedral
- carbon in the CH_2 group — four regions of electron density; tetrahedral

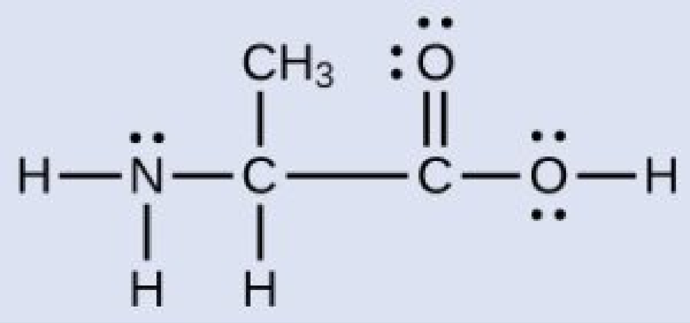
- carbon in the CO_2 group — three regions of electron density; trigonal planar
- oxygen in the OH group — four regions of electron density; tetrahedral

The local structures:

- nitrogen — three bonds, one lone pair; trigonal pyramidal
- carbon in the CH_2 group — four bonds, no lone pairs; tetrahedral
- carbon in the CO_2 group — three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen in the OH group — two bonds, two lone pairs; bent (109°)

Exercise 11.6f

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Check Your Answer[6]

Exercise 11.6g

Practice using the following PhET simulation Molecular Shapes:

Example 11.6g

Molecular Simulation

Use the molecular shape simulator in Exercise 11.6g. It allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called "electron geometry" in the simulator) and/or molecular structure (called "molecular shape" in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$\mathbf{H-C\equiv N}$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Exercise 11.6h

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Check Your Answer[7]

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = \mathrm{Qr}$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude (Figure 11.6m). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

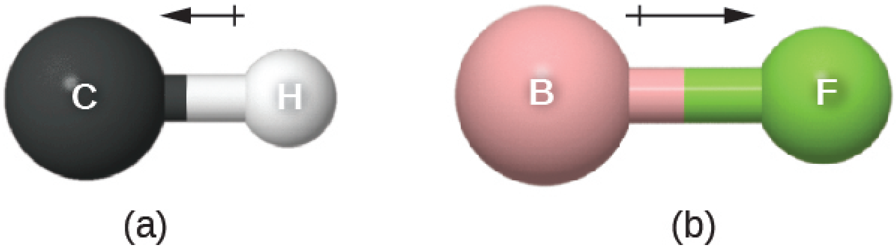


Figure 11.6m (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 11.6n). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 11.6n), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

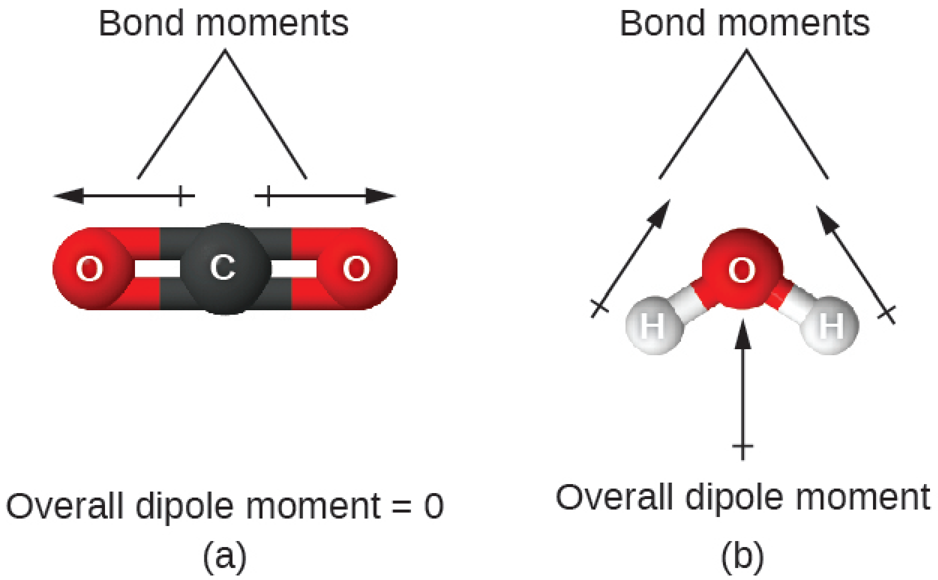


Figure 11.6n The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The OCS molecule (Figure 11.6o) has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

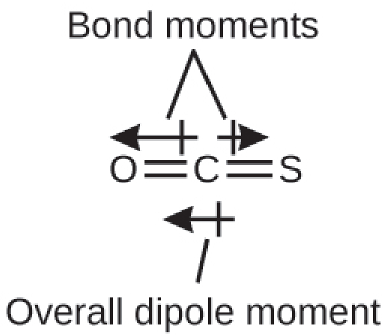


Figure 11.6o The OCS molecule is shown to have a linear structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl (Figure 11.6p), is another example of a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the

C–H bond, and the bond moments do not completely cancel each other. All of the dipoles have a downward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:

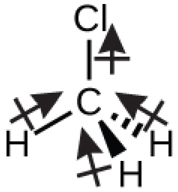


Figure 11.6p The CH_3Cl structure has a tetrahedral shape and represents a polar molecule (credit: *Chemistry (OpenStax)*,CC BY 4.0).

When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3 (Figure 11.6q). A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:

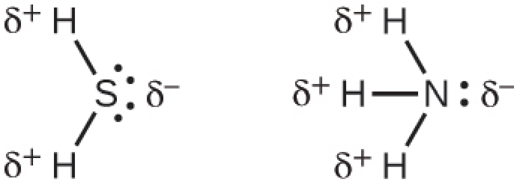


Figure 11.6q H_2S and NH_3 represent structures where the dipoles do not cancel due to the lone pair of electrons (credit: *Chemistry (OpenStax)*,CC BY 4.0).

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Exercise 11.6i

Check Your Learning Exercise (Text Version)
From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

a. C, F, H, N, O
b. Br, Cl, F, H, I
c. F, H, O, P, S
d. Al, H, Na, O, P
e. Ba, H, N, O, As

Check Your Answer[8]

Source: "Exercise 11.6i" is adapted from "Exercise 4.2-7" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate. We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

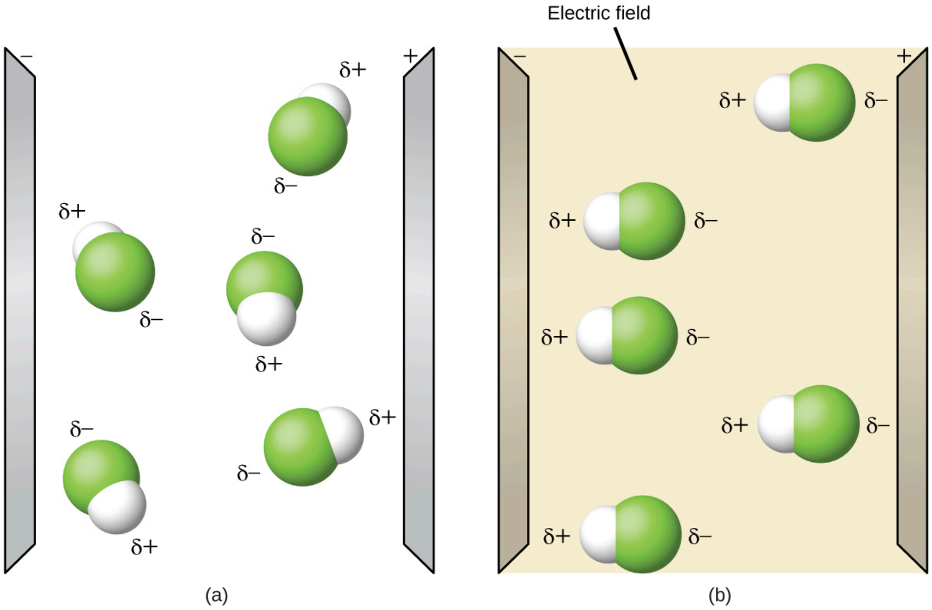


Figure 11.6r (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction (credit: *Chemistry (OpenStax)*,CC BY 4.0).

Exercise 11.6J

Practice using the following PhET simulation: Molecule Polarity.

Example 11.6h

Polarity Simulations

Open the molecule polarity simulation and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 11.6r.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 11.6K

Determine the partial charges that will give the largest possible bond dipoles.

Check Your Answer[9]

Links to Interactive Learning Tools

Explore VSEPR Theory from the Physics Classroom.

Attribution & References

Except where otherwise noted, this page is adapted JR van Haarlem from "4.7 Molecular Structure and Polarity" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*

Notes

1. The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.
2. Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.
3. electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal
4. The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.
5. electron pair geometry: trigonal bipyramidal; molecular structure: linear
6. electron-pair geometries: nitrogen––tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)
7. Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.
8. (a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O
9. The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

CHAPTER 11 - SUMMARY

11.1 Ionic Bonding

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

11.2 Covalent Bonding

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

11.3 Lewis Symbols and Structures

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

11.4 Formal Charges and Resonance

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

11.5 Molecular Structure and Polarity

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

11.6 Molecular Structure and Polarity

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from "4.1 Ionic Bonding", "4.2 Covalent Bonding", "4.3 Lewis Symbols and Structures", "4.4 Lewis Symbols and Structures", "4.5 Formal Charges and Resonance", "4.6 Strengths of Ionic and Covalent Bonds" and "4.7 Molecular Structure and Polarity" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul

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CHAPTER 11 - REVIEW

11.1 Ionic Bonding

1. Does a cation gain protons to form a positive charge or does it lose electrons? **Check Answer:** [1]
2. Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and $SO_4{}^{2-}$ ions. Explain why a sample of iron(III) sulfate is uncharged.
3. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co? **Check Answer:** [2]
4. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?
5. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
   a. P
   b. Mg
   c. Al
   d. O
   e. Cl
   f. Cs

   Check Answer: [3]
6. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
   a. I
   b. Sr
   c. K
   d. N
   e. S
   f. In
7. Write the electron configuration for each of the following ions:
   a. As^{3-}
   b. I^-
   c. Be^{2+}
   d. Cd^{2+}
   e. O^{2-}
   f. Ga^{3+}
   g. Li^+

   - h. N^{3-}
   - i. Sn^{2+}
   - j. Co^{2+}
   - k. Fe^{2+}
   - l. As^{3+}

   Check Answer: [4]

8. Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):
   - a. Cl
   - b. Na
   - c. Mg
   - d. Ca
   - e. K
   - f. Br
   - g. Sr
   - h. F
9. Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:
   - a. Al
   - b. Br
   - c. Sr
   - d. Li
   - e. As
   - f. S

   Check Answer: [5]
10. From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

11.2 Covalent Bonding

1. Why is it incorrect to speak of a molecule of solid NaCl? **Check Answer:** [6]
2. What information can you use to predict whether a bond between two atoms is covalent or ionic?
3. Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:
   - a. Cl_2CO
   - b. MnO

   c. NCl_3
   d. $CoBr_2$
   e. K_2S
   f. CO
   g. CaF_2
   h. HI
   i. CaO
   j. IBr
   k. CO_2

   Check Answer: [7]

4. Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.
5. From its position in the periodic table, determine which atom in each pair is more electronegative:
   a. Br or Cl
   b. N or O
   c. S or O
   d. P or S
   e. Si or N
   f. Ba or P
   g. N or K

   Check Answer: [8]

6. From its position in the periodic table, determine which atom in each pair is more electronegative:
   a. N or P
   b. N or Ge
   c. S or F
   d. Cl or S
   e. H or C
   f. Se or P
   g. C or Si
7. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:
   a. C, F, H, N, O
   b. Br, Cl, F, H, I
   c. F, H, O, P, S
   d. Al, H, Na, O, P
   e. Ba, H, N, O, As

   Check Answer: [9]

8. From their positions in the periodic table, arrange the atoms in each of the following series in order of

increasing electronegativity:
   - a. As, H, N, P, Sb
   - b. Cl, H, P, S, Si
   - c. Br, Cl, Ge, H, Sr
   - d. Ca, H, K, N, Si
   - e. Cl, Cs, Ge, H, Sr

9. Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom? **Check Answer:** [10]
10. Which is the most polar bond?
    - a. C–C
    - b. C–H
    - c. N–H
    - d. O–H
    - e. Se–H
11. Identify the more polar bond in each of the following pairs of bonds:
    - a. HF or HCl
    - b. NO or CO
    - c. SH or OH
    - d. PCl or SCl
    - e. CH or NH
    - f. SO or PO
    - g. CN or NN

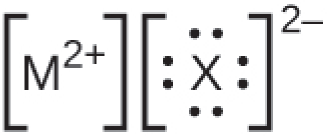
      Check Answer: [11]
12. Which of the following molecules or ions contain polar bonds?
    - a. O_3
    - b. S_8
    - c. O22−O22−
    - d. NO3−NO3−
    - e. CO_2
    - f. H_2S
    - g. BH4−BH4−

11.3 Lewis Symbols and Structures

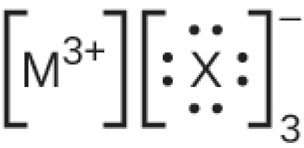
1. Write the Lewis symbols for each of the following ions:
   - a. As^{3-}
   - b. I^{-}

   c. Be^{2+}
   d. O^{2-}
   e. Ga^{3+}
   f. Li^{+}
   g. N^{3-}
   Check Answer: [12]
2. Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:
   a. Cl
   b. Na
   c. Mg
   d. Ca
   e. K
   f. Br
   g. Sr
   h. F
3. Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:
   a. MgS
   b. Al_2O_3
   c. $GaCl_3$
   d. K_2O
   e. Li_3N
   f. KF
   Check Answer: [13]
4. In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

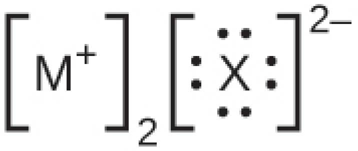
(a)



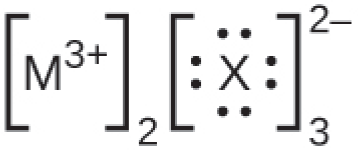
(b)



(c)



(d)



5. Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor. **Check Answer:** [14]
6. Write Lewis structures for the following:
   a. H_2
   b. HBr
   c. PCl_3
   d. SF_2
   e. H_2CCH_2
   f. HNNH
   g. H_2CNH
   h. NO^-
   i. N_2
   j. CO
   k. CN^-
7. Write Lewis structures for the following:
   a. O_2
   b. H_2CO
   c. AsF_3
   d. ClNO
   e. $SiCl_4$
   f. H_3O^+
   g. NH_4^+
   h. BF_4^-
   i. HCCH
   j. ClCN
   k. C_2^{2+}

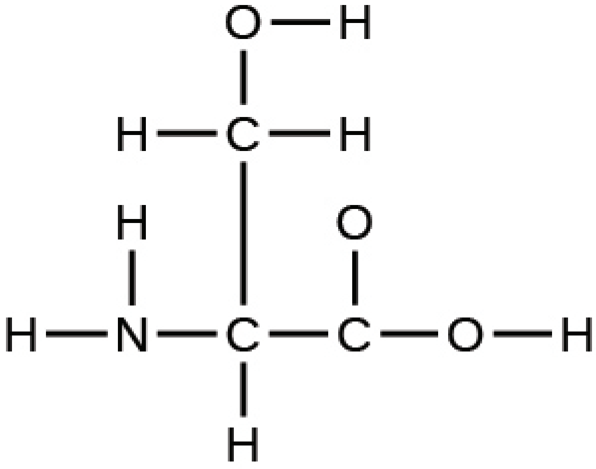
   Check Answer: [15]
8. Write Lewis structures for the following:

   a. ClF_3
   b. PCl_5
   c. BF_3
   d. PF_6^-
9. Write Lewis structures for the following:
   a. SeF_6
   b. XeF_4
   c. $SeCl_3^+$
   d. Cl_2BBCl_2 (contains a B–B bond)
   Check Answer: [16]
10. Write Lewis structures for:
   a. PO_4^{3-}
   b. ICl_4^-
   c. SO_3^{2-}
   d. HONO
11. Correct the following statement: "The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms."
   Check Answer: [17]
12. Write Lewis structures for the following molecules or ions:
   a. SbH_3
   b. XeF_2
   c. Se_8 (a cyclic molecule with a ring of eight Se atoms)
13. Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.
   Check Answer: [18]
14. Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.
15. Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene. **Check Answer:** [19]
16. Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:
   a. $1s^2 2s^2 2p^5$
   b. $1s^2 2s^2 2p^6 3s^2$

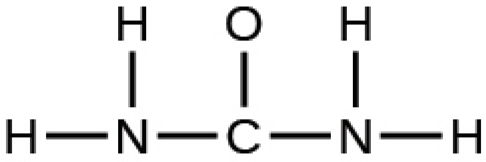
c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
e. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

17. The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.
Check Answer: [20]

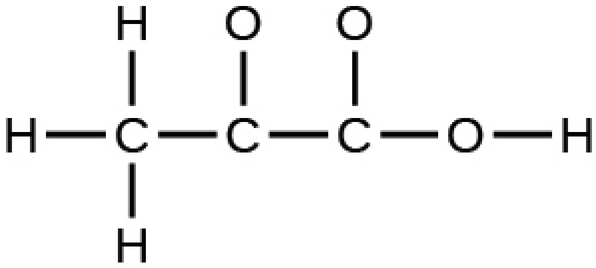
(a) the amino acid serine:



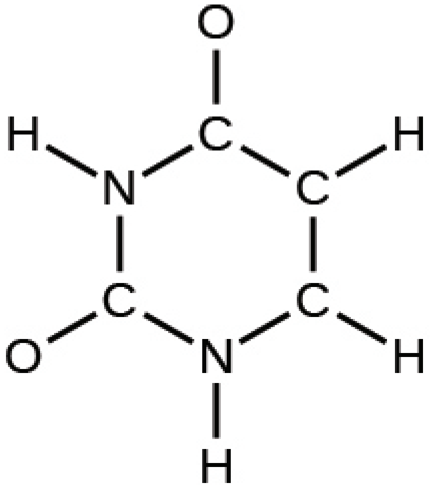
(b) urea:



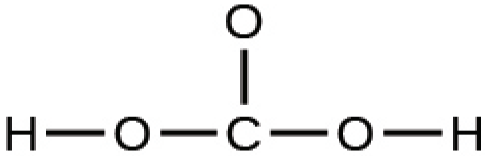
(c) pyruvic acid:



(d) uracil:



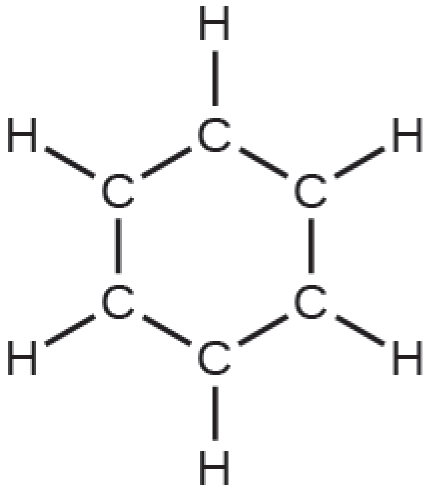
(e) carbonic acid:



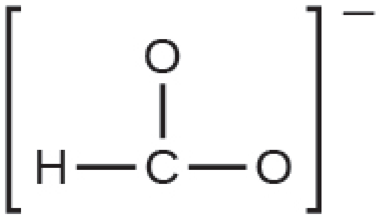
18. A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.
19. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound. **Check Answer:** [21]
20. Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.
21. How are single, double, and triple bonds similar? How do they differ? **Check Answer:** [22]

11.4 Formal Charges and Resonance

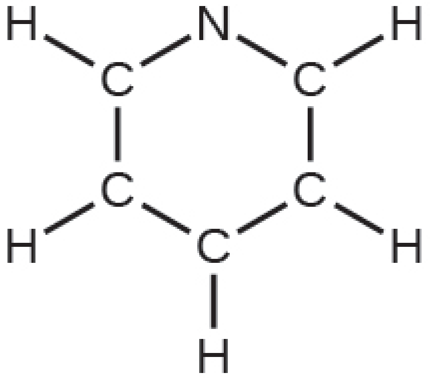
1. Write resonance forms that describe the distribution of electrons in each of these molecules or ions.
   a. selenium dioxide, OSeO
   b. nitrate ion, NO_3^-
   c. nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)
   d. benzene, C_6H_6:



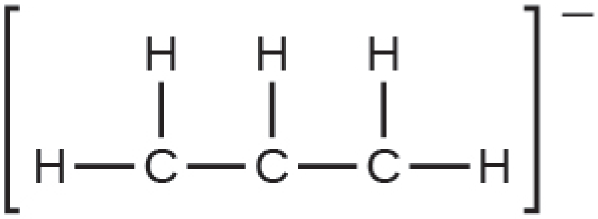
e. the formate ion:



2. Write resonance forms that describe the distribution of electrons in each of these molecules or ions.
   a. sulfur dioxide, SO_2
   b. carbonate ion, CO_3^{2-}
   c. hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

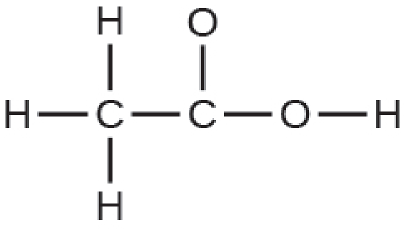


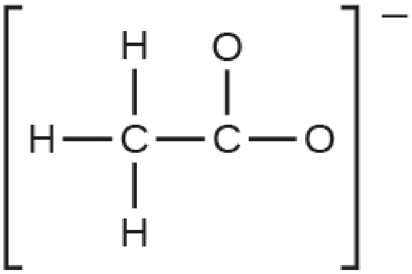
   d. pyridine:
   e. the allyl ion:



Check Answer: [23]

3. Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.
4. Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^-. **Check Answer:** [24]
5. In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:





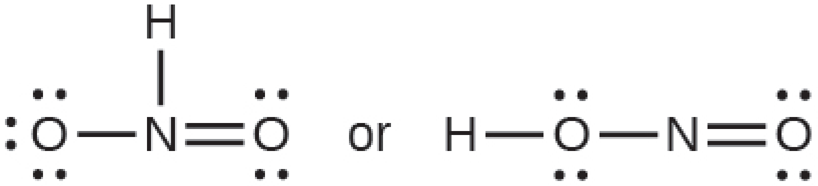
6. Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.
   a. CO_2
   b. CO

   Check Answer: [25]
7. Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.
8. Determine the formal charge of each element in the following:
   a. HCl
   b. CF_4
   c. PCl_3
   d. PF_5

   Check Answer: [26]
9. Determine the formal charge of each element in the following:
   a. H_3O^+
   b. SO_4^{2-}

   c. NH_3
   d. O_2^{2-}
   e. H_2O_2
10. Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5. **Check Answer:** [27]
11. Calculate the formal charge of each element in the following compounds and ions:
   a. F_2CO
   b. NO^-
   c. BF_4^-
   d. $SnCl_3^-$
   e. H_2CCH_2
   f. ClF_3
   g. SeF_6
   h. PO_4^{3-}
12. Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:
   a. O_3
   b. SO_2
   c. NO_2^-
   d. NO_3^-
   Check Answer: [28]
13. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?
14. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH? **Check Answer:** [29]
15. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?
16. Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges? **Check Answer:** [30]
17. Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:
   a. IF
   b. IF_3
   c. IF_5
   d. IF_7
18. Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound. **Check Answer:** [31]

19. Which of the following structures would we expect for nitrous acid? Determine the formal charges:

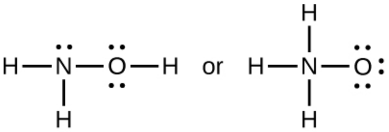


20. Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur. **Check Answer:** [32]

11.5 Strengths of Ionic and Covalent Bonds

1. Which bond in each of the following pairs of bonds is the strongest?
   a. C–C or C=C
   b. C–N or C≡N
   c. C≡O or C=O
   d. H–F or H–Cl
   e. C–H or O–H
   f. C–N or C–O
2. Using the bond energies in Table 11.5a, determine the approximate enthalpy change for each of the following reactions:
   a. $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
   b. $CH_4(g) + I_2(g) \longrightarrow CH_3I(g) + HI(g)$
   c. $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

   Check Answer: [33]
3. Using the bond energies in Table 11.5a, determine the approximate enthalpy change for each of the following reactions:
   a. $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g)$
   b. $H_2C = CH_2(g) + H_2(g) \longrightarrow H_3CCH_3(g)$
   c. $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$
4. When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



Check Answer: [34]

5. How does the bond energy of HCl(*g*) differ from the standard enthalpy of formation of HCl(*g*)?

6. Using the standard enthalpy of formation data in Appendix H, show how the standard enthalpy of formation of HCl(*g*) can be used to determine the bond energy. **Check Answer:** [35]
7. Using the standard enthalpy of formation data in Appendix H, calculate the bond energy of the carbon-sulfur double bond in CS_2.
8. Using the standard enthalpy of formation data in Appendix H, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$? **Check Answer:** [36]
9. Using the standard enthalpy of formation data in Appendix H, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?
10. Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:

Check Answer: [37]

11. Use the bond energy to calculate an approximate value of Δ*H* for the following reaction. Which is the more stable form of FNO_2?

12. Use principles of atomic structure to answer each of the following:[38]
    a. The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.
    b. The lattice energy of CaO(*s*) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.
    c. Given these ionization values in the data table below, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

   d. The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.
   Check Answer: [39]

13. The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.
14. For which of the following substances is the least energy required to convert one mole of the solid into separate ions?
   a. MgO
   b. SrO
   c. KF
   d. CsF
   e. MgF_2
   Check Answer: [40]
15. The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $\mathrm{M}(s) + \mathrm{X}_2(g) \longrightarrow \mathrm{MX}_2(s)$. For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.
   a. a large radius vs. a small radius for M^{+2}
   b. a high ionization energy vs. a low ionization energy for M
   c. an increasing bond energy for the halogen
   d. a decreasing electron affinity for the halogen
   e. an increasing size of the anion formed by the halogen
16. The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.
   Check Answer: [41]
17. Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^{+} have similar radii; O^{2-} and F^{-} have similar radii. Explain your choices.
   1. MgO or MgSe
   2. LiF or MgO
   3. Li_2O or LiCl
   4. Li_2Se or MgO
18. Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and K^{+} have similar radii; S^{2-} and Cl^{-} have similar radii. Explain your choices.
   a. K_2O or Na_2O
   b. K_2S or BaS

   c. KCl or BaS
   d. BaS or $BaCl_2$

   Check Answer: [42]

19. Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?
   a. MgO
   b. SrO
   c. KF
   d. CsF
   e. MgF_2
20. Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?
   a. K_2S
   b. K_2O
   c. CaS
   d. Cs_2S
   e. CaO

   Check Answer: [43]

21. The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol, 924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

11.6 Molecular Structure and Polarity

1. Explain why the HOH molecule is bent, whereas the HBeH molecule is linear. **Check Answer:** [44]
2. What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?
3. Explain the difference between electron-pair geometry and molecular structure. **Check Answer:** [45]
4. Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?
5. Explain how a molecule that contains polar bonds can be nonpolar. **Check Answer:** [46]
6. As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?
7. Predict the electron pair geometry and the molecular structure of each of the following molecules or

ions:

   a. SF_6
   b. PCl_5
   c. BeH_2
   d. CH_3^+

   Check Answer: [47]

8. Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:
   a. IF_6^+
   b. CF_4
   c. BF_3
   d. SiF_5^-
   e. $BeCl_2$
9. What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?
   a. ClF_5
   b. ClO_2^-
   c. $TeCl_4^{2-}$
   d. PCl_3
   e. SeF_4
   f. PH_2^-

   Check Answer: [48]
10. Predict the electron pair geometry and the molecular structure of each of the following ions:
    a. H_3O^+
    b. PCl_4^-
    c. $SnCl_3^-$
    d. $BrCl_4^-$
    e. ICl_3
    f. XeF_4
    g. SF_2
11. Identify the electron pair geometry and the molecular structure of each of the following molecules:
    a. ClNO (N is the central atom)
    b. CS_2
    c. Cl_2CO (C is the central atom)
    d. Cl_2SO (S is the central atom)
    e. SO_2F_2 (S is the central atom)
    f. XeO_2F_2 (Xe is the central atom)

   g. $ClOF_2^+$ (Cl is the central atom)

   Check Answer: [49]

12. Predict the electron pair geometry and the molecular structure of each of the following:
   a. IOF_5 (I is the central atom)
   b. $POCl_3$ (P is the central atom)
   c. Cl_2SeO (Se is the central atom)
   d. $ClSO^+$ (S is the central atom)
   e. F_2SO (S is the central atom)
   f. NO_2^-
   g. SiO_4^{4-}
13. Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?
   a. ClF_5
   b. ClO_2^-
   c. $TeCl_4^{2-}$
   d. PCl_3
   e. SeF_4
   f. PH_2^-
   g. XeF_2

   Check Answer: [50]
14. Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?
   a. H_3O^+
   b. PCl_4^-
   c. $SnCl_3^-$
   d. $BrCl_4^-$
   e. ICl_3
   f. XeF_4
   g. SF_2
15. Which of the following molecules have dipole moments?
   a. CS_2
   b. SeS_2
   c. CCl_2F_2
   d. PCl_3 (P is the central atom)
   e. $ClNO$ (N is the central atom)

   Check Answer: [51]
16. Identify the molecules with a dipole moment:

   a. SF_4
   b. CF_4
   c. Cl_2CCBr_2
   d. CH_3Cl
   e. H_2CO
17. The molecule XF_3 has a dipole moment. Is X boron or phosphorus? **Check Answer:** [52]
18. The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?
19. Is the Cl_2BBCl_2 molecule polar or nonpolar? **Check Answer:** [53]
20. There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.
21. Describe the molecular structure around the indicated atom or atoms:
   a. the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]
   b. the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]
   c. the oxygen atom in hydrogen peroxide, HOOH
   d. the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]
   e. the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]
   f. the central oxygen atom in the ozone molecule, O_3
   g. each of the carbon atoms in propyne, CH_3CCH
   h. the carbon atom in Freon, CCl_2F_2
   i. each of the carbon atoms in allene, H_2CCCH_2
   Check Answer: [54]
22. Draw the Lewis structures and predict the shape of each compound or ion:
   a. CO_2
   b. NO_2^-
   c. SO_3
   d. SO_3^{2-}
23. A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape. **Check Answer:** [55]
24. A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.
25. Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:
   a. CS_3^{2-}
   b. CS_2
   c. CS

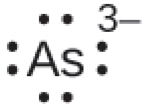
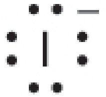
   d. predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions
   Check Answer: [56]

26. What is the molecular structure of the stable form of FNO_2? (N is the central atom.)
27. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure? **Check Answer:** [57]
28. Use the Molecule Polarity simulation to perform the following exercises for a two-atom molecule:
    a. Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
    b. With a partial positive charge on A, turn on the electric field and describe what happens.
    c. With a small partial negative charge on A, turn on the electric field and describe what happens.
    d. Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.
29. Use the Molecule Polarity simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.
    a. Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.
    b. Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.
    c. Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.
    Check Answer: [58]
30. Use the Molecule Shape simulator to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

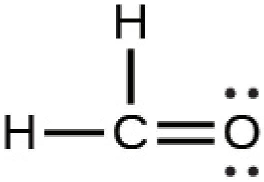
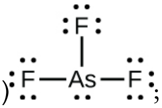
Attribution & References

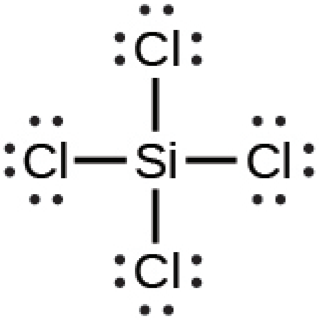
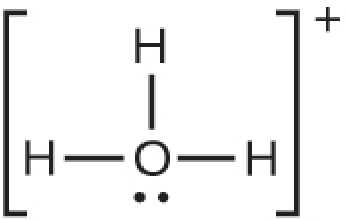
Except where otherwise noted, this page is adapted by JR van Haarlem from "4.1 Ionic Bonding", "4.2 Covalent Bonding", "4.3 Lewis Symbols and Structures", "4.4 Lewis Symbols and Structures", "4.5 Formal Charges and Resonance", "4.6 Strengths of Ionic and Covalent Bonds" and "4.7 Molecular Structure and Polarity" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*. / Extracted exercises from each section for this page.

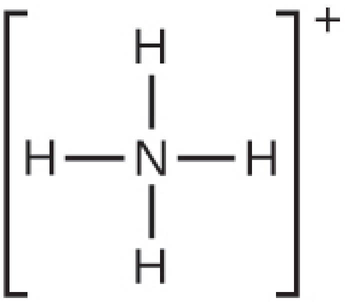
Notes

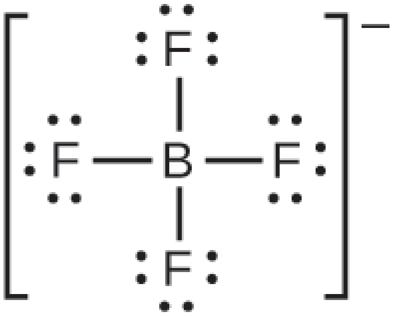
1. The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.
2. P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.
3. (a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}
4. (a) $[Ar]4s^23d^{10}4p^6$; (b) $[Kr]4d^{10}5s^25p^6$ (c) $1s^2$ (d) $[Kr]4d^{10}$; (e) $[He]2s^22p^6$; (f) $[Ar]3d^{10}$; (g) $1s^2$ (h) $[He]2s^22p^6$ (i) $[Kr]4d^{10}5s^2$ (j) $[Ar]3d^7$ (k) $[Ar]3d^6$, (l) $[Ar]3d^{10}4s^2$
5. (a) $1s^22s^22p^63s^23p^1$; Al^{3+}: $1s^22s^22p^6$; (b) $1s^22s^22p^63s^23p^63d^{10}4s^24p^5$; $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$; (c) $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$; Sr^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$; (d) $1s^22s^1$; Li^+: $1s^2$; (e) $1s^22s^22p^63s^23p^63d^{10}4s^24p^3$; $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$; (f) $1s^22s^22p^63s^23p^4$; $1s^22s^22p^63s^23p^6$
6. NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.
7. ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)
8. (a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N
9. (a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O
10. N, O, F, and Cl
11. (a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN
12. 1. (a) eight electrons:  ; (b) eight electrons:  ; (c) no electrons Be^{2+}; (d) eight electrons:  ; (e) no electrons Ga^{3+}; (f) no electrons Li^+; (g) eight electrons: 
13. 3. (a)  ; (b)  ; (c)  ; (d)  >; (e)  ; (f) 
14. 

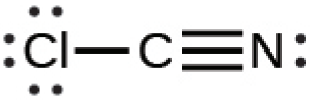
15. (a)  In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

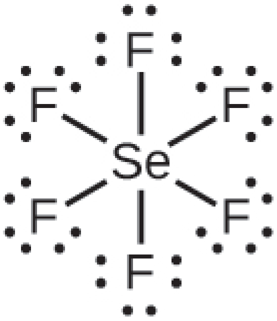
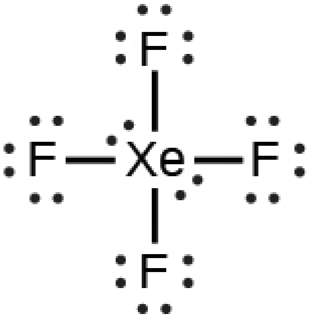
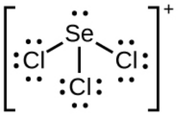
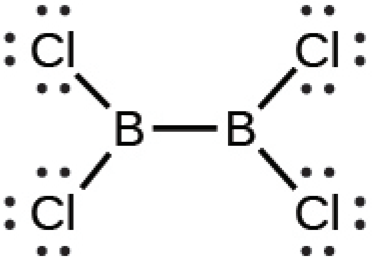
(b)  ; (c)  ; (d)  ;

(e)  ; (f)  ; (g)

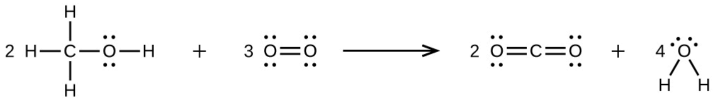
 ; (h)

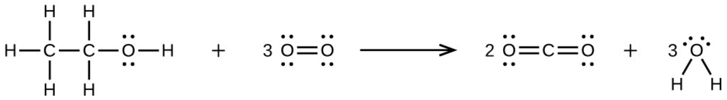
 ; (i)  ; (j)

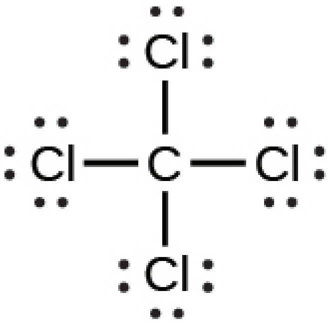
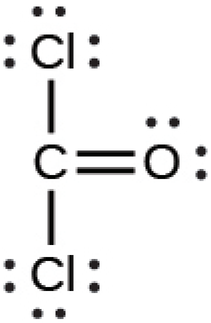
 ; (k) 

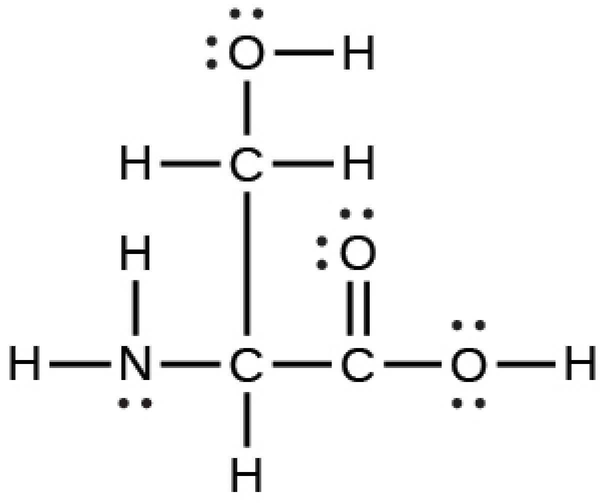
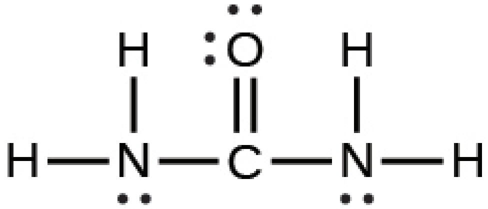
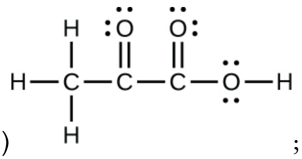
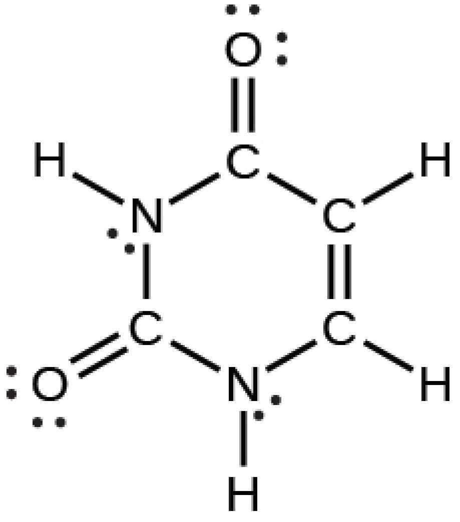
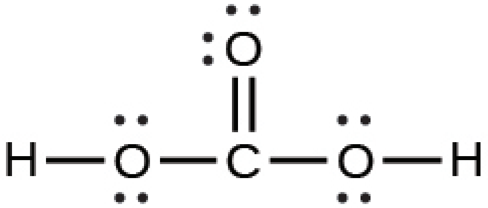
16. (a) SeF_6:  ; (b) XeF_4:  ; (c) $SeCl_3^+$:  ; (d) Cl_2BBCl_2: 

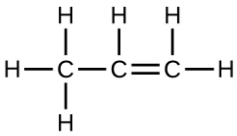
17. Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.



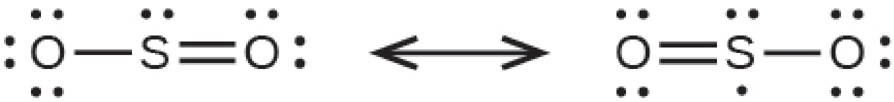
18. 

19.  

20. (a)  ; (b)  ; (c)  ; (d)  ; (e) 

21. 

22. Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

23. (a) 

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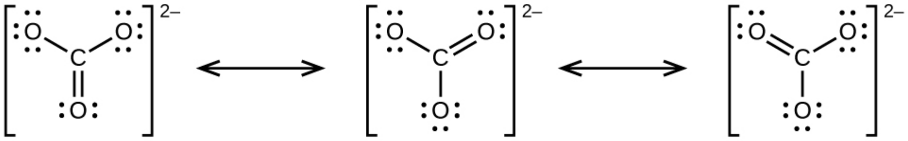

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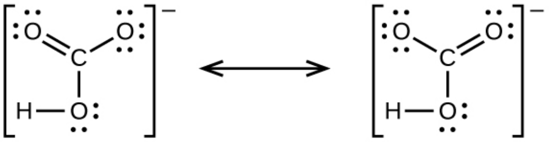

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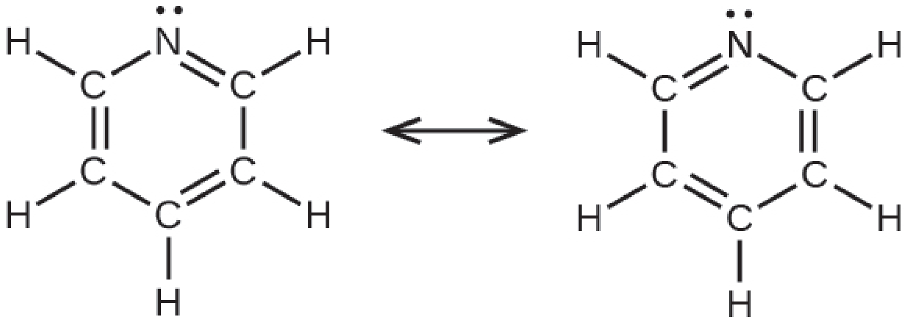

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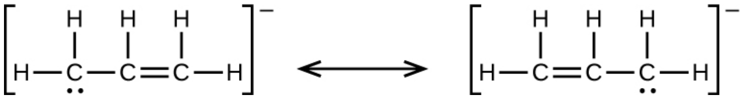

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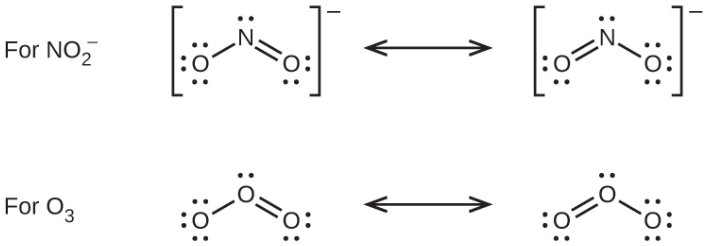
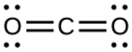


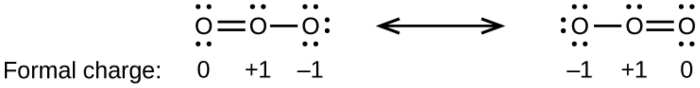
25. (a) 

(b)  CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

26. (a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl 0; (d) P: 0, F: 0

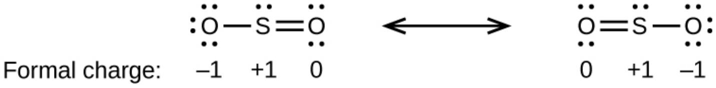
27. Cl in Cl_2: 0; Cl in $BeCl_2$: 0; Cl in ClF_5: 0

28. (a)

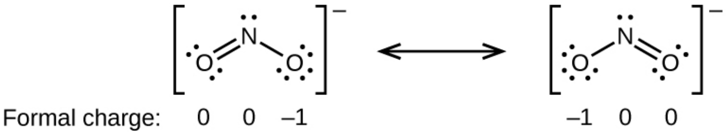


;

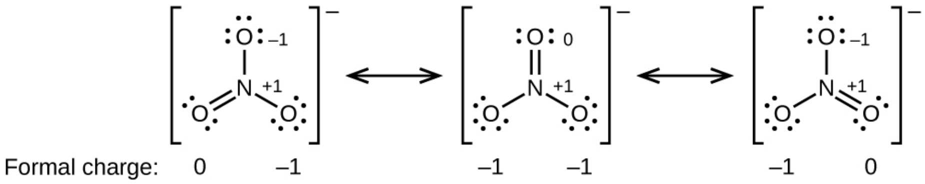
(b)



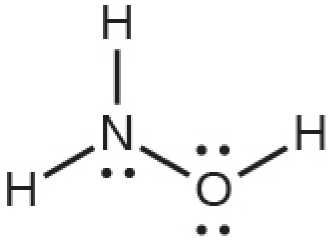
; (c)



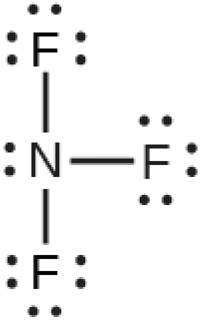
; (d)



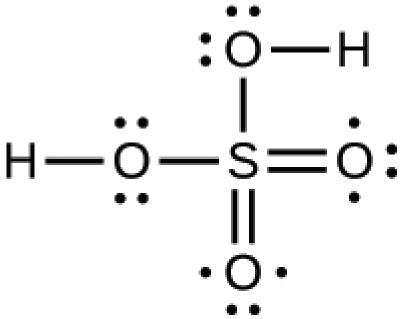
29. HOCl



30. The structure that gives zero formal charges is consistent with the actual structure:



31. NF3;



32.

33. (a) −114 kJ; (b) 30 kJ; (c) −1055 kJ

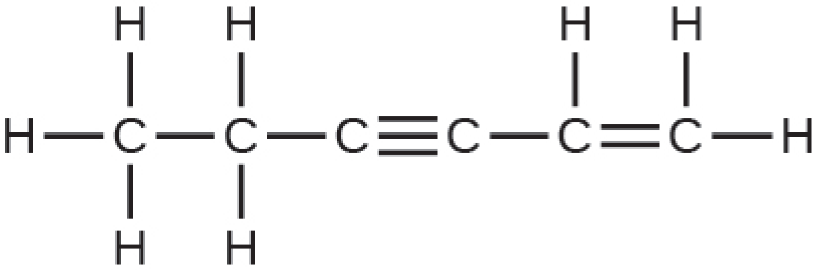
34. The greater bond energy is in the figure on the left. It is the more stable form.

35.

$$\begin{array}{ll}
\mathrm{HCl}(g) \longrightarrow \frac{1}{2}\mathrm{H}_2(g) + \frac{1}{2}\mathrm{Cl}_2(g) & \Delta H_1^\circ = -\Delta H^\circ_{\mathrm{f[HCl}(g)]} \\
\frac{1}{2}\mathrm{H}_2(g) \longrightarrow \mathrm{H}(g) & \Delta H_2^\circ = \Delta H^\circ_{\mathrm{f[H}(g)]} \\
\frac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{Cl}(g) & \Delta H_3^\circ = \Delta H^\circ_{\mathrm{f[Cl}(g)]} \\
\hline
\mathrm{HCl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g) & \Delta H^\circ_{298} = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ
\end{array}$$

$$\begin{aligned} D_{\text{HCl}} = \Delta H^\circ_{298} = \quad & -\Delta H^\circ_{\text{f[HCl}(g)]} + \Delta H^\circ_{\text{f[H}(g)]} + \Delta H^\circ_{\text{f[Cl}(g)]} \\ & = -(-92.307 \text{ kJ}) + 217.97 \text{ kJ} + 121.3 \text{ kJ} \\ & = 431.6 \text{ kJ} \end{aligned}$$

36. The S–F bond in SF_4 is stronger.

37.  The C–C single bonds are longest.

38. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

39. (a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower *n* = 3 level, which is much smaller in radius. (b) The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion. (c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level. (d) In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

40. (d)

41. 4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

42. (a) Na_2O; Na^+ has a smaller radius than K^+; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

43. (e)

44. The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

45. Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

46. As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

47. (a) Both the electron geometry and the molecular structure are octahedral. (b) Both the electron geometry and the molecular structure are trigonal bipyramid. (c) Both the electron geometry and the molecular structure are linear. (d) Both the electron geometry and the molecular structure are trigonal planar.

48. (a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

49. (a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

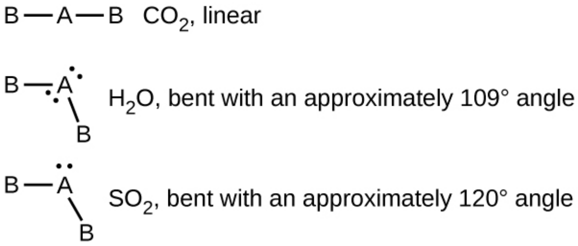
50. All of these molecules and ions contain polar bonds. Only ClF_5, ClO_2^-, PCl_3, SeF_4, and PH_2^- have dipole moments.

51. SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

52. P

53. nonpolar

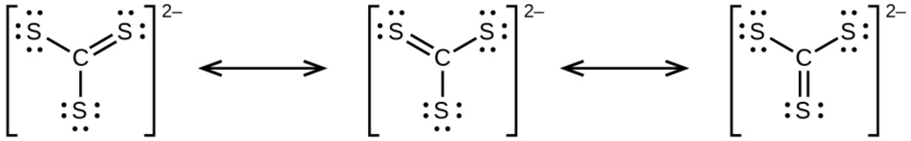
54. (a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) CH_3CCH - first carbon on left is tetrahedral, middle carbon and carbon on right are linear; (h) tetrahedral; (i) H_2CCCH_2 - middle carbon is linear; carbons on left and right are trigonal planar

55. 

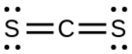
CO_2, linear

H_2O, bent with an approximately 109° angle

SO_2, bent with an approximately 120° angle

56. (a) 

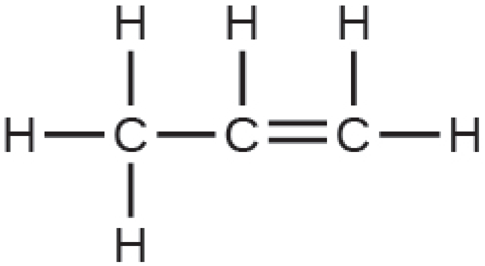
;

(b) 

; (c) 

; (d) CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

57. The Lewis structure is made from three units, but the atoms must be rearranged:



58. The molecular dipole points away from the hydrogen atoms.

CHAPTER 12: GASES

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The relationships of Pressure, Temperature and Volume as they pertain to gases
- The nature of gas particle movement

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Mathematics
- Stoichiomentry

Figure 12a The hot air inside these balloons is less dense than the surrounding cool air. This results in a buoyant force that causes the balloons to rise when their guy lines are untied. (credit: work by Elif Tütüncü, CC BY-SA 4.0)

We are surrounded by an ocean of gas—the atmosphere—and many of the properties of gases are familiar to us from our daily activities. Heated gases expand, which can make a hot air balloon rise (Figure 12.a) or cause a blowout in a bicycle tire left in the sun on a hot day.

Gases have played an important part in the development of chemistry. In the seventeenth and eighteenth centuries, many scientists investigated gas behaviour, providing the first mathematical descriptions of the behaviour of matter.

In this chapter, we will examine the relationships between gas temperature, pressure, amount, and volume.

We will study a simple theoretical model and use it to analyze the experimental behaviour of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

Attribution & References

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12.1 GAS PRESSURE

Learning Objectives

By the end of this section, you will be able to:

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure 12.1a). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

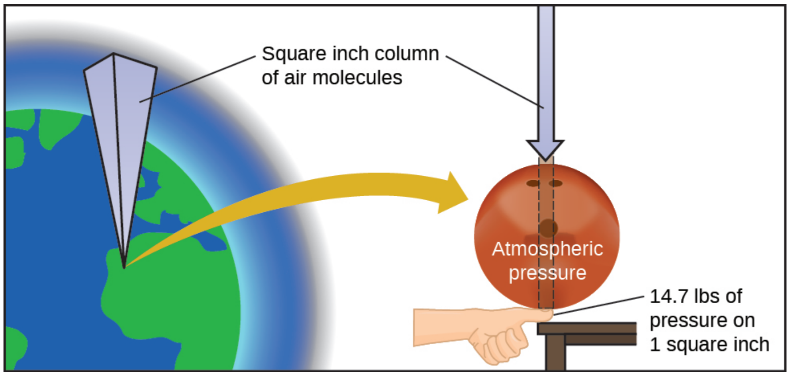


Figure 12.1a The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail (credit: *Chemistry (OpenStax)*,CC BY 4.0).

Watch **Railroad tank car vacuum implosion (1 min)**

Watch **Crush a 55 gallon drum with air pressure (4 mins)**

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is *twice* the usual pressure, and the sensation is unpleasant.

In general, **pressure** is defined as the force exerted on a given area: $P = \frac{F}{A}$. Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which would be more likely to fall through thin ice in Figure 12.1b—the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

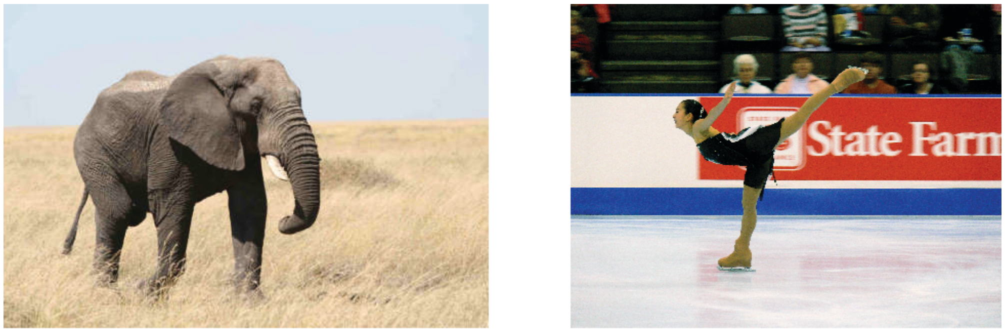
$$\text{pressure per elephant foot} = 14,000\frac{\text{lb}}{\text{elephant}} \times \frac{1\ \text{elephant}}{4\ \text{feet}} \times \frac{1\ \text{foot}}{250\ \text{in}^2} = 14\ \text{lb/in}^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\ \text{skater}}{2\ \text{blades}} \times \frac{1\ \text{blade}}{2\ \text{in}^2} = 30\ \text{lb/in}^2$$

Even though the elephant is more than one hundred times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall though thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\ \text{skater}}{2\ \text{feet}} \times \frac{1\ \text{foot}}{30\ \text{in}^2} = 2\ \text{lb/in}^2$$



(a) (b)

Figure 12.1b Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze, CC BY 2.0; credit b: modification of work by Ryosuke Yagi, CC BY 2.0)

Watch Describing the invisible properties of gas – Brian Bennett (4 mins)

Exercise 12.1a

Practice using the following PhET simulation: Gases Intro

The SI unit of pressure is the **pascal (Pa)**, with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere (atm)**, which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 12.1a provides some information on these and a few other common units for pressure measurements

Table 12.1a Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	1 Pa = 1 N/m^2 recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi
atmosphere (atm)	1 atm = 101,325 Pa air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly) commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa used by aviation industry, also some weather reports
torr	$1 \text{ torr} = \frac{1}{760} \text{ atm}$ named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr

Exercise 12.1b

Check Your Learning Exercise (Text Version)
Canadian tire pressure gauges are marked in units of kilopascals. The reading on this type of pressure gauge for 32 psi will be

Check Your Answer[1]

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Example 12.1a

Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 12.1a.

a. $29.2\ \cancel{\text{in Hg}} \times \dfrac{25.4\ \cancel{\text{mm}}}{1\ \cancel{\text{in}}} \times \dfrac{1\ \text{torr}}{1\ \cancel{\text{mm}}\ \text{Hg}} = 742\ \text{torr}$

b. $742\ \cancel{\text{torr}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.976\ \text{atm}$

c. $742\ \cancel{\text{torr}} \times \dfrac{101.325\ \text{kPa}}{760\ \cancel{\text{torr}}} = 98.9\ \text{kPa}$

d. $98.9\ \cancel{\text{kPa}} \times \dfrac{1000\ \cancel{\text{Pa}}}{1\ \cancel{\text{kPa}}} \times \dfrac{1\ \cancel{\text{bar}}}{100,000\ \cancel{\text{Pa}}} \times \dfrac{1000\ \text{mbar}}{1\ \cancel{\text{bar}}} = 989\ \text{mbar}$

Exercise 12.1c

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimetres of mercury, in kilopascals, and in bar?

Check Your Answer[2]

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a

barometer (Figure 12.1d). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

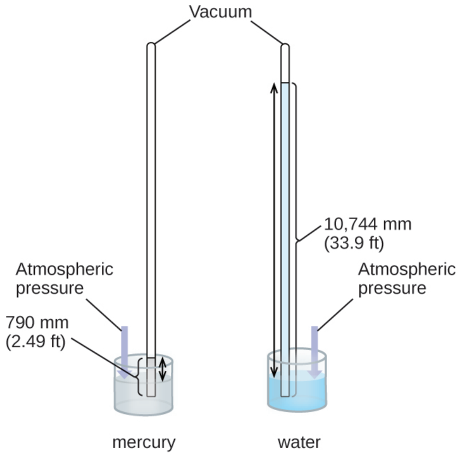


Figure 12.1d In a barometer, the height, *h*, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The **torr** was originally intended to be a unit equal to one millimetre of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as **hydrostatic pressure**, p:

$$p = h\rho g$$

where h is the height of the fluid, ρ is the density of the fluid, and g is acceleration due to gravity.

Exercise 12.1d

Check Your Learning Exercise (Text Version)
Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?

Check Your Answer[3]

Source: “Exercise 12.1b” is adapted from “Exercise 8.1-3” in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 12.1b

Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = 13.6 g/cm^3.

Solution

The hydrostatic pressure is given by $p = h\rho g$, with h = 760 mm, ρ = 13.6 g/cm^3, and g = 9.81 m/s^2. Plugging these values into the equation and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325 N/\mathrm{m}^2 = 101,325 \frac{\mathrm{kg} \cdot \mathrm{m/s}^2}{\mathrm{m}^2} = 101,325 \frac{\mathrm{kg}}{\mathrm{m} \cdot \mathrm{s}^2}$$

$$\begin{aligned} p &= (760\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}) \times (\frac{13.6\ \mathrm{g}}{1\ \mathrm{cm}^3} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \frac{(100\ \mathrm{cm})^3}{(1\ \mathrm{m})^3}) \times (\frac{9.81\ \mathrm{m}}{1\ \mathrm{s}^2}) \\ &= (0.760\ \mathrm{m})(13,600\ \mathrm{kg/m}^3)(9.81\ \mathrm{m/s}^2) = 1.01 \times 10^5\ \mathrm{kg/ms}^2 = 1.01 \times 10^5\ N/\mathrm{m}^2 \\ &= 1.01 \times 10^5\ \mathrm{Pa} \end{aligned}$$

Exercise 12.1e

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Check Your Answer[4]

Exercise 12.1f

Check Your Learning Exercise (Text Version)
A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

Check Your Answer[5]

Source: "Exercise 12.1f" is adapted from "Exercise 8.1-5" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

A **manometer** is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure 12.1e) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

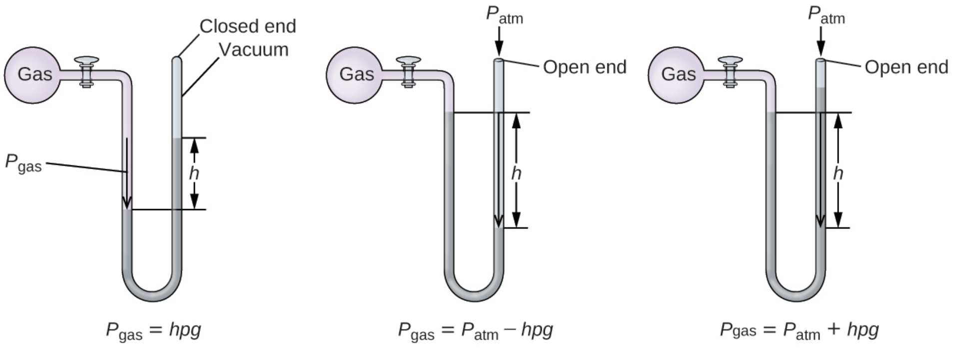


Figure 12.1e A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (*h*) is a measure of the pressure. Mercury is usually used because of its large density (credit: *Chemistry (OpenStax)*,CC BY 4.0).

Exercise 12.1g

Check Your Learning Exercise (Text Version)
The pressure of a sample of gas is measured at sea level with an open-end mercury manometer and height (*h*) in open end is measured as 13.7cm below the gas height in the closed end. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in

a. mm Hg
b. atm
c. kPa

Check Your Answer[6]

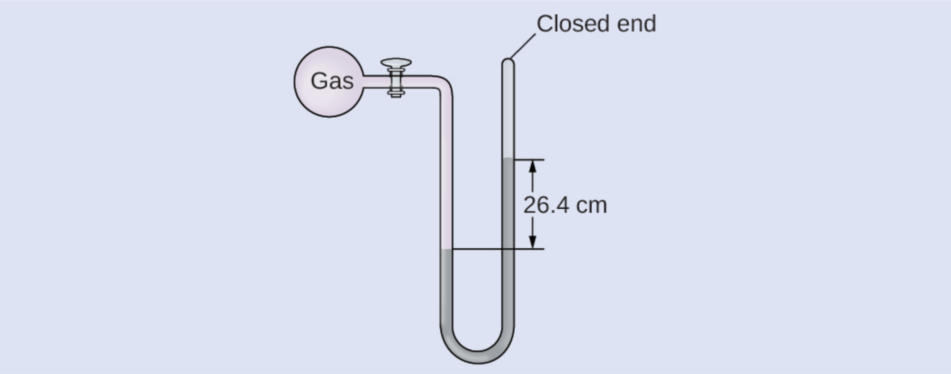
Source: "Exercise 12.1g" is adapted from "8.1 Example 4" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 12.1c

Calculation of Pressure Using a Closed-End Manometer

The pressure of a sample of gas is measured with a closed-end manometer, as shown to the right. The liquid in the manometer is mercury. Determine the pressure of the gas in:

a. torr
b. Pa
c. bar



Solution

The pressure of the gas is equal to a column of mercury of height 26.4 cm. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 26.4 cm Hg, or mercury.) We could use the equation $p = h\rho g$ as in Example 12.1b, but it is simpler to just convert between units using Table 12.1a.

a. $26.4\ \cancel{\text{cm Hg}} \times \dfrac{10\ \cancel{\text{mm Hg}}}{1\ \cancel{\text{mm Hg}}} \times \dfrac{1\ \text{torr}}{1\ \cancel{\text{mm Hg}}} = 264\ \text{torr}$

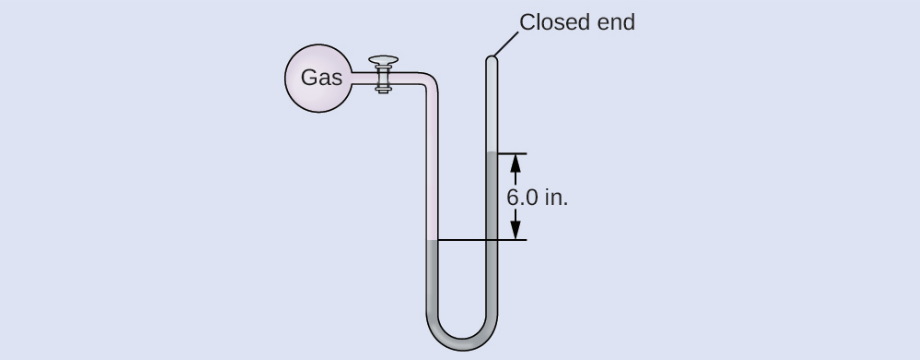
b. $264\ \cancel{\text{torr}} \times \dfrac{1\ \cancel{\text{atm}}}{760\ \cancel{\text{torr}}} \times \dfrac{101,325\ \text{Pa}}{1\ \cancel{\text{atm}}} = 35,200\ \text{Pa}$

c. $35,200\ \cancel{\text{Pa}} \times \dfrac{1\ \text{bar}}{100,000\ \cancel{\text{Pa}}} = 0.352\ \text{bar}$

Exercise 12.1h

The pressure of a sample of gas is measured with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

a. torr
b. Pa
c. bar



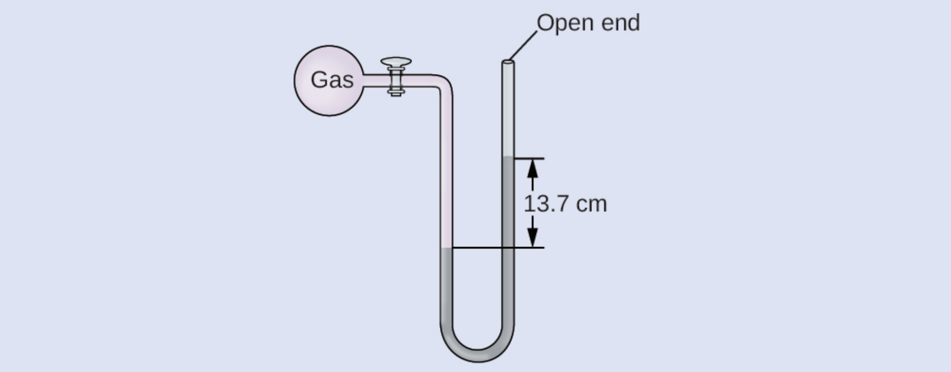
Check Your Answer[7]

Example 12.1d

Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown to the right. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



Solution

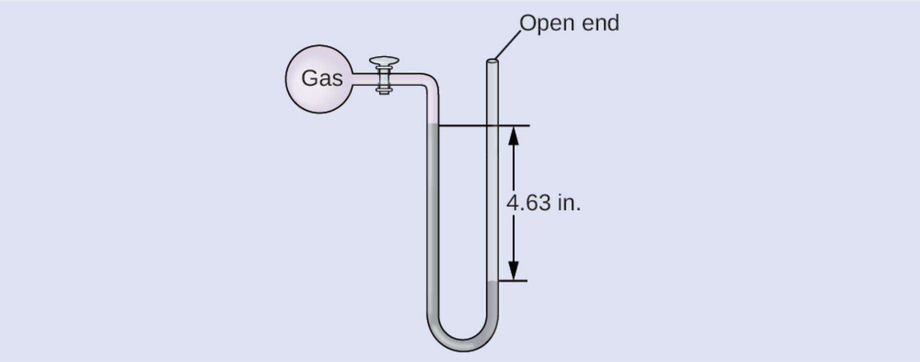
The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

a. In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg
b. $897\ \cancel{\text{mm Hg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mm Hg}}} = 1.18\ \text{atm}$
c. $1.18\ \cancel{\text{atm}} \times \dfrac{101.325\ \text{kPa}}{1\ \cancel{\text{atm}}} = 1.20 \times 10^2\ \text{kPa}$

Exercise 12.1i

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown to the right. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



Check Your Answer[8]

Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = “pulse”). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 12.1f). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff’s pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart’s ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimetres of mercury (mm Hg).

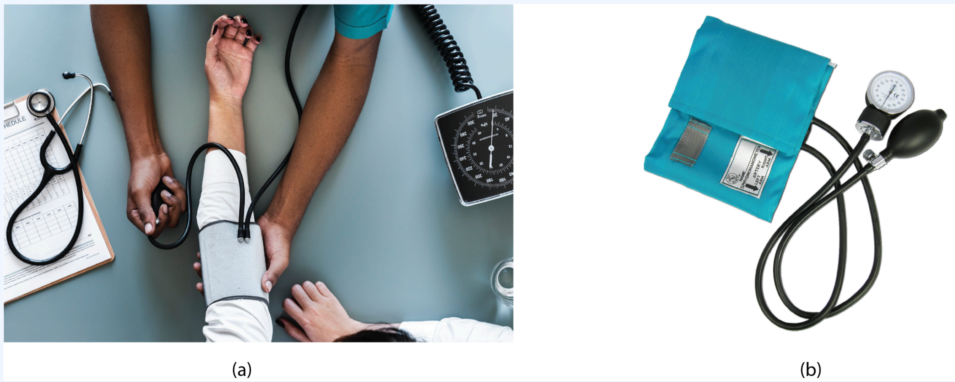


Figure 12.1f (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: work by rawpixel.com, CC0; credit b: work by Medisave UK, CC BY 2.0)

METEOROLOGY, CLIMATOLOGY, AND ATMOSPHERIC SCIENCE

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modelled, and analyzed in weather centres worldwide.

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 12.1h: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

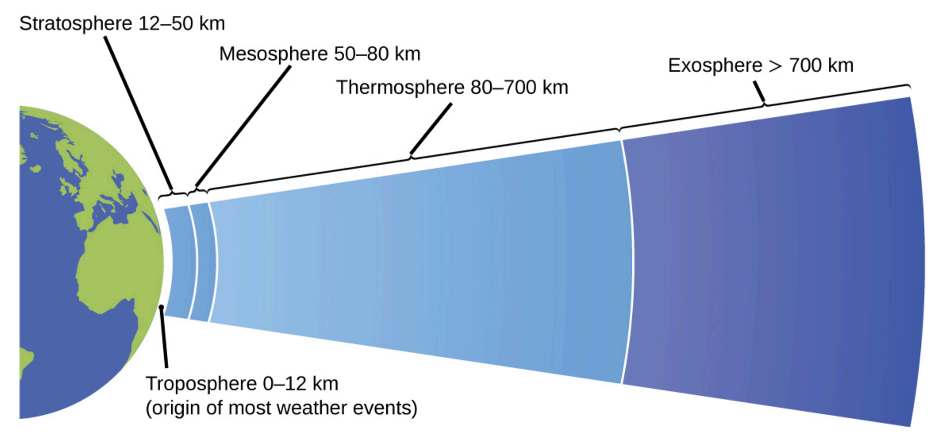


Figure 12.1g Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere (credit: *Chemistry (OpenStax)*,CC BY 4.0).

Links to Interactive Learning Tools

Explore Pressure Concepts from the Physics Classroom.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Attribution & References

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Notes

1. 2.2×10^2 kPa
2. 0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar
3. Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.
4. 10.3 m
5. 0.809 atm and 82.0 kPa
6. (a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa
7. (a) ~150 torr; (b) ~20,000 Pa; (c) ~0.20 bar
8. (a) 642 mm Hg; (b) 0.845 atm; (c) 85.6 kPa

12.2 RELATING PRESSURE, VOLUME, AMOUNT, AND TEMPERATURE: THE IDEAL GAS LAW

Learning Objectives

By the end of this section, you will be able to:

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure 12.2a), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.

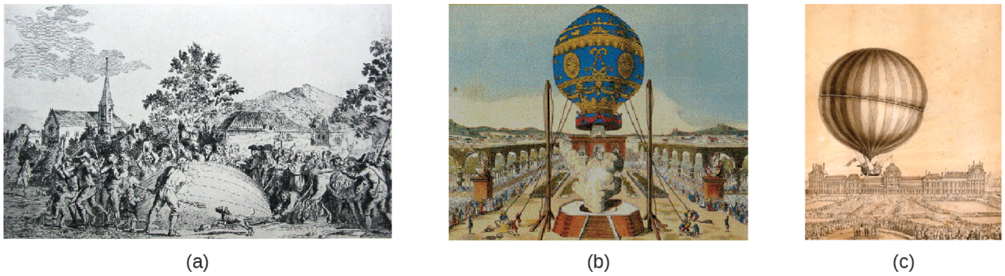

Figure 12.2a In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris. (credit: a) work by unknown, PD; b) work by Claude Louis Desrais, PD; c) work by unknown, digitally enhanced by RawPixel, CC BY-SA 4.0)

Pressure and Temperature: Gay-Lussac's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure 12.2b) and the pressure increases.

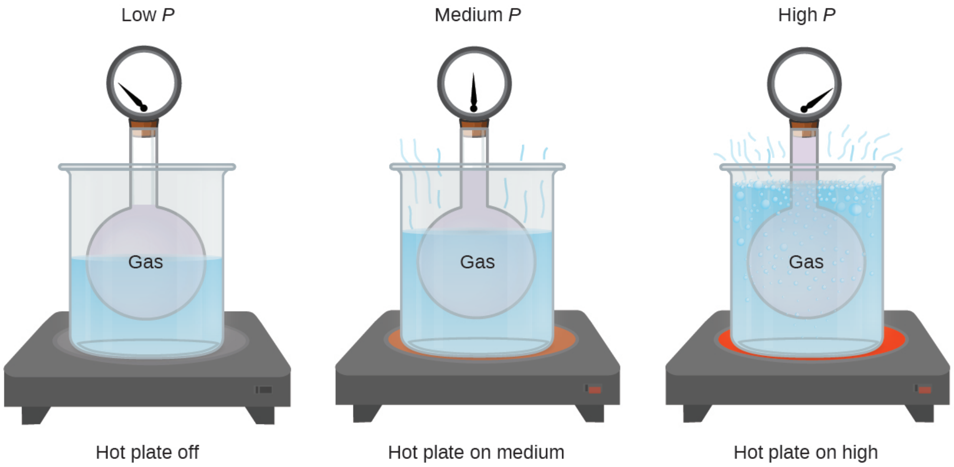

Figure 12.2b The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases (credit: *Chemistry (OpenStax)*,CC BY 4.0).

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure 12.2c. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held* *constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
–150	173	36.0
–100	223	46.4
–50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0

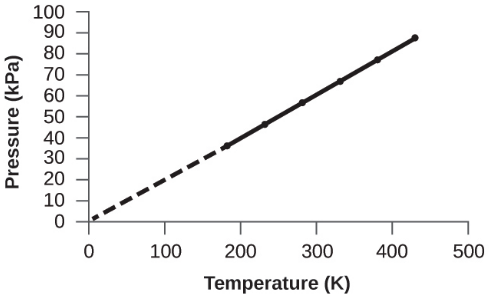

Figure 12.2c For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero (credit: Chemistry (OpenStax),CC BY 4.0).

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the P–T relationship for gases is known as either **Amontons' law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where ∝ means "is proportional to," and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example 12.2a

Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)
b. We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons'/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives: $P_2 = \frac{360 \text{ kPa} \times 323 \cancel{\text{K}}}{297 \cancel{\text{K}}} = 390 \text{ kPa}$

Exercise 12.2a

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Check Your Answer[1]

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

Watch Liquid Nitrogen Experiments: The Balloon (3 mins)

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in .

Temperature (°C)	Temperature (K)	Volume (L)
−3	270	22
−23	250	21
−53	220	18
−162	111	9

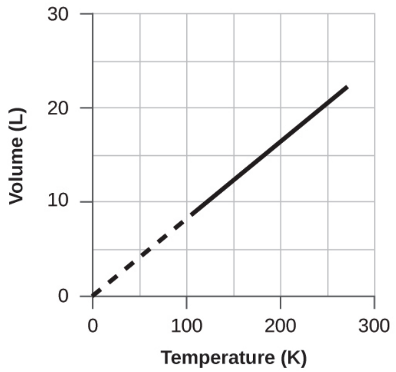

Figure 12.2d The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero (credit: *Chemistry (OpenStax)*,CC BY 4.0).

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles' law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles' law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \propto T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T \text{ or } V_1/T_1 = V_2/T_2$$

with k being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = k), and as seen with the P–T relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

Example 12.2b

Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which menas that} \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

Rearranging and solving gives: $V_2 = \dfrac{0.300 \text{ L} \times 303 \cancel{\text{K}}}{283 \cancel{\text{K}}} = 0.321 \text{ L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Exercise 12.2b

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Check Your Answer[2]

Example 12.2c

Measuring Temperature with a Volume Change

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that} \frac{150.0 \text{ cm}^3}{273.15 \text{ K}} = \frac{131.7 \text{ cm}^3}{T_2}$$

Rearrangement gives $T_2 = \dfrac{131.7 \cancel{\text{cm}^3} \times 273.15 \text{ K}}{150.0 \cancel{\text{cm}^3}} = 239.8 \text{ K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

Exercise 12.2c

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Check Your Answer[3]

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in

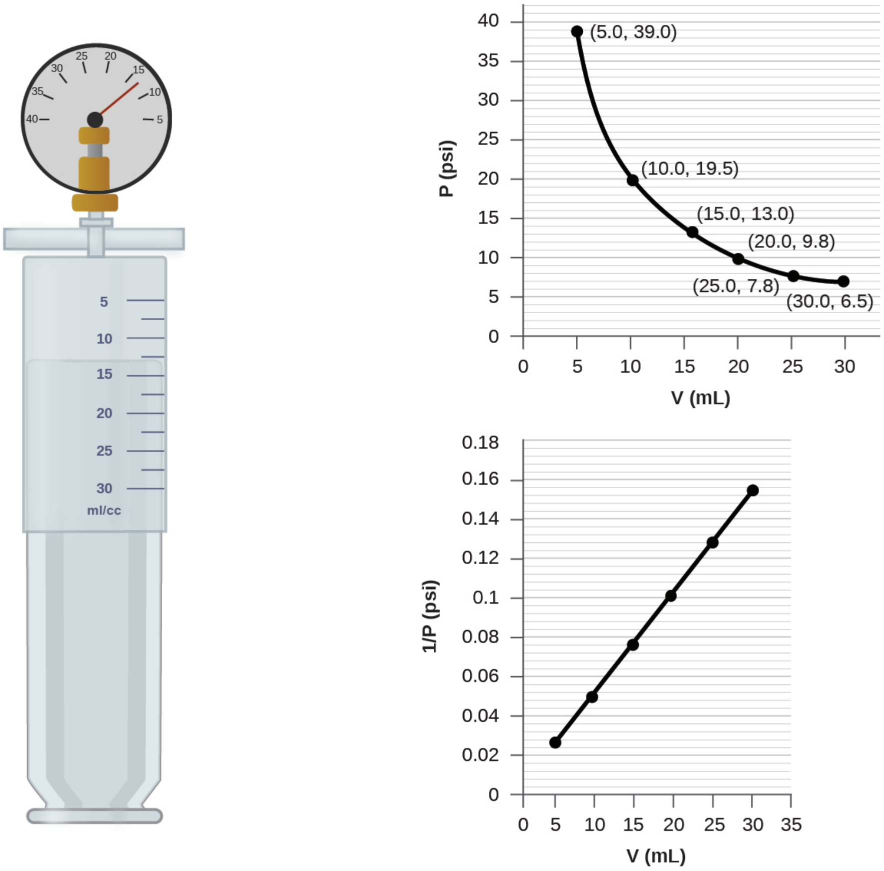

Figure 12.2e. When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since *P* and *V* are inversely proportional, a graph of 1/*P* vs. *V* is linear (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Unlike the P–T and V–T relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto \ 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1V_1 = P_2V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure $(\dfrac{1}{P})$ versus the volume (V), or the inverse of volume $(\dfrac{1}{V})$ versus the pressure (P). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to “linearize” their data. If we plot P versus V, we obtain a hyperbola (see Figure 12.2f).

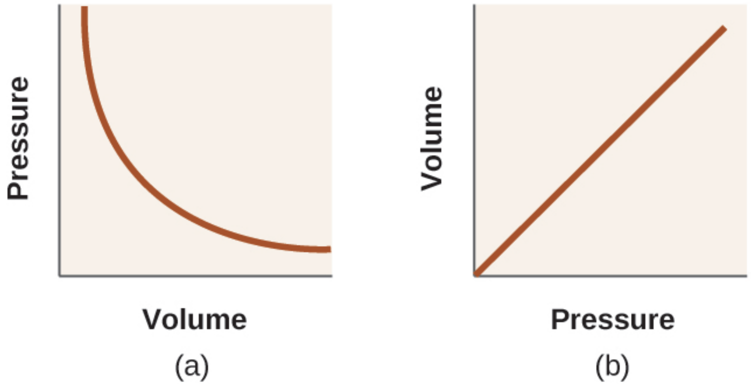

Figure 12.2f The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of ($1/P$) vs. V is linear (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example 12.2d

Volume of a Gas Sample

The sample of gas in Figure 12.2e has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the P–V graph in Figure 12.2e
b. the $\frac{1}{p}$ vs. V graph in Figure 12.2e
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

a. Estimating from the P–V graph gives a value for P somewhere around 27 psi.
b. Estimating from the $\frac{1}{P}$ versus V graph give a value of about 26 psi.
c. From Boyle's law, we know that the product of pressure and volume (PV) for a given sample of

gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$ Solving:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \cancel{\text{mL}}}{7.5 \cancel{\text{mL}}} = 26 \text{ psi}$$

It was more difficult to estimate well from the *P–V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Exercise 12.2d

The sample of gas in Figure 12.2e has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P–V* graph in Figure 12.2e
b. the $\frac{1}{P}$ vs. *V* graph in Figure 12.2e
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Check Your Answer[4]

Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 12.2g).

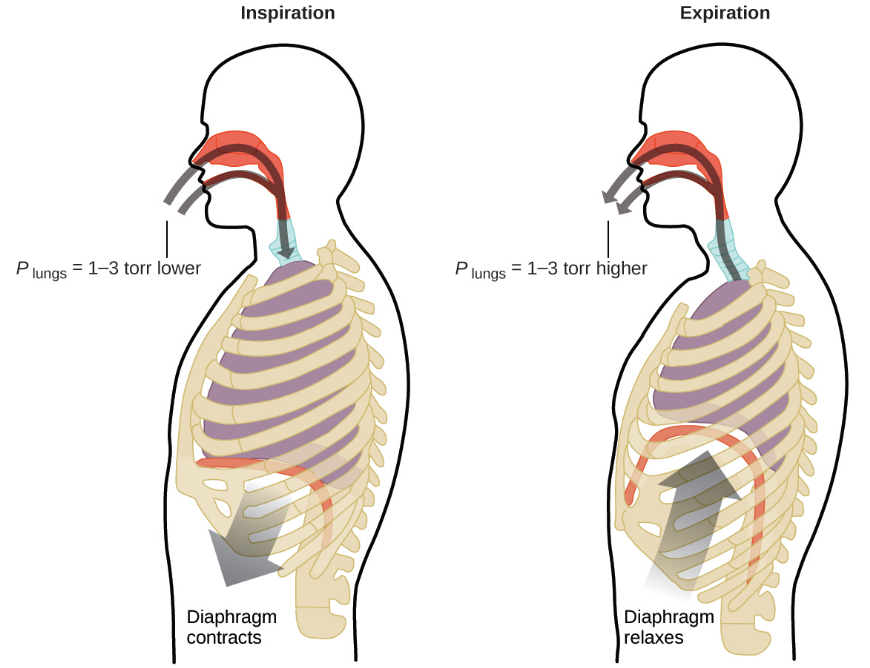

Figure 12.2g Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behaviour of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant*.

In equation form, this is written as:

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as P versus n, and n versus T.

Exercise 12.2e

Practice using the following PhET simulation: Gas Properties

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons' law: $\frac{P}{T}$ = constant at constant V and n
- Charles' law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law: $\frac{V}{n}$ = constant at constant P and T

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.314 kPa L mol^{-1} K^{-1}.

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behaviour* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behaviour, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behaviour observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 12.2e

Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

We must rearrange $PV = nRT$ to solve for V: $V = \frac{nRT}{P}$

If we choose to use R = 0.08206 L atm mol^{-1} K^{-1}, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the "right" units:

$$n = 655\ \cancel{\text{g CH}_4} \times \frac{1\ \text{mol}}{16.043\ \cancel{\text{g CH}_4}} = 40.8\ \text{mol}$$

$$T = 25\ {}^\circ\text{C} + 273 = 298\ \text{K}$$

$$P = 745\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.980\ \text{atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8\ \cancel{\text{mol}})(0.08206\text{L}\ \cancel{\text{atm mol}^{-1}\ \text{K}^{-1}})(298\ \cancel{\text{K}})}{0.980\ \cancel{\text{atm}}} = 1.02 \times 10^3\ \text{L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Exercise 12.2f

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Check Your Answer[5]

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law

Example 12.2f

Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 12.2h). If the water temperature is 27 °C, how many litres of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?

Figure 12.2h Scuba divers use compressed air to breathe while underwater (credit: work by Subro89, CC BY-SA 4.0).

Solution

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \longrightarrow \frac{(153\ \mathrm{atm})(13.2\ \mathrm{L})}{(300\ \mathrm{K})} = \frac{(3.13\ \mathrm{atm})(V_2)}{(310\ \mathrm{K})}$$

Solving for V_2:

$$V_2 = \frac{(153\ \cancel{\mathrm{atm}})(13.2\ \mathrm{L})(310\ \cancel{\mathrm{K}})}{(300\ \cancel{\mathrm{K}})(3.13\ \cancel{\mathrm{atm}})} = 667\ \mathrm{L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behaviour is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good “ballpark” estimate.)

Exercise 12.2g

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Check Your Answer[6]

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 12.2i) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.

Figure 12.2i Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: work by Kyle Taylor, CC BY 2.0)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as "atmospheres absolute" or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body's air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Watch **The ABC's of gas: Avogadro, Boyle, Charles – Brian Bennett**

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa). At STP, an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** (Figure 12.2j).

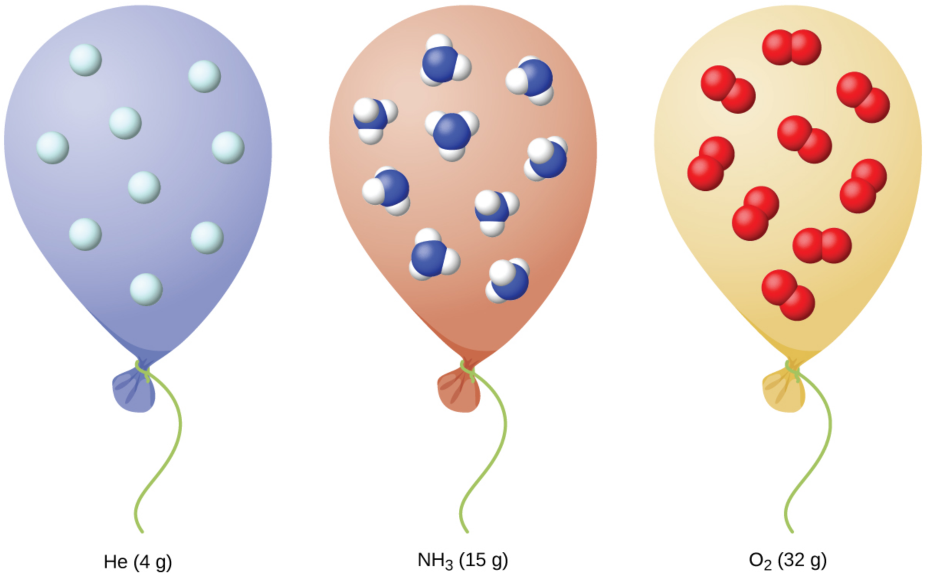

Figure 12.2j Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 12.2h

Check Your Learning Exercise (Text Version)
A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can?

Check Your Answer[7]

Source: "Exercise 12.2h" is adapted from "Exercise 8.2-10" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Links to Interactive Learning Tools

Explore Volume-Temperature Gas Law from the Physics Classroom.

Explore Pressure-Volume Gas Law from the Physics Classroom.

Explore Pressure-Temperature Gas Law from the Physics Classroom.

Key Equations

- $PV = nRT$

Attribution & References

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Notes

1. 400 torr
2. 21.6 mL
3. 635 mL
4. (a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow
5. 350 bar
6. 0.193 L
7. 3.4×10^3 torr

12.3 EFFUSION AND DIFFUSION OF GASES

Learning Objectives

By the end of this section, you will be able to:

- Define and explain effusion and diffusion
- State Graham's law and use it to compute relevant gas properties

If you have ever been in a room when a piping hot pizza was delivered, you have been made aware of the fact that gaseous molecules can quickly spread throughout a room, as evidenced by the pleasant aroma that soon reaches your nose. Although gaseous molecules travel at tremendous speeds (hundreds of metres per second), they collide with other gaseous molecules and travel in many different directions before reaching the desired target. At room temperature, a gaseous molecule will experience billions of collisions per second. The **mean free path** is the average distance a molecule travels between collisions. The mean free path increases with decreasing pressure; in general, the mean free path for a gaseous molecule will be hundreds of times the diameter of the molecule

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called **diffusion** (shown in Figure 12.3a). The gaseous atoms or molecules are, of course, unaware of any concentration gradient, they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in Figure 12.3a. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no *net* transfer of molecules occurs).

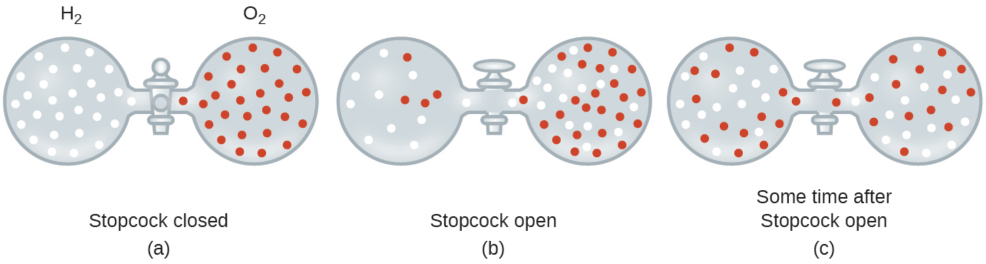

Figure 12.3a (a) Two gases, H_2 and O_2, are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas, H_2, passes through the opening faster than O_2, so just after the stopcock is opened, more H_2 molecules move to the O_2 side than O_2 molecules move to the H_2 side. (c) After a short time, both the slower-moving O_2 molecules and the faster-moving H_2 molecules have distributed themselves evenly on both sides of the vessel (credit: *Chemistry (OpenStax)*, CC BY 4.0).

We are often interested in the **rate of diffusion**, the amount of gas passing through some area per unit time:

$$\text{rate of diffusion} = \frac{\text{amount of gas passing through an area}}{\text{unit of time}}$$

The diffusion rate depends on several factors: the concentration gradient (the increase or decrease in concentration from one point to another); the amount of surface area available for diffusion; and the distance the gas particles must travel. Note also that the time required for diffusion to occur is inversely proportional to the rate of diffusion, as shown in the rate of diffusion equation.

A process involving movement of gaseous species similar to diffusion is **effusion**, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (Figure 12.3b). Although diffusion and effusion rates both depend on the molar mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.

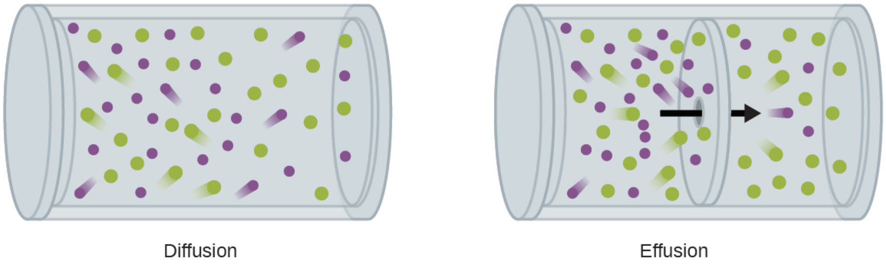

Figure 12.3b Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance traveled between collisions. Effectively, this means that only one particle passes through at a time (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If a mixture of gases is placed in a container with porous walls, the gases effuse through the small openings in the walls. The lighter gases pass through the small openings more rapidly (at a higher rate) than the heavier ones (Figure 12.3c). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated

Graham's law of effusion: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*:

$$\text{rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

This means that if two gases A and B are at the same temperature and pressure, the ratio of their effusion rates is inversely proportional to the ratio of the square roots of the masses of their particles:

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{\mathcal{M}_\text{B}}}{\sqrt{\mathcal{M}_\text{A}}}$$

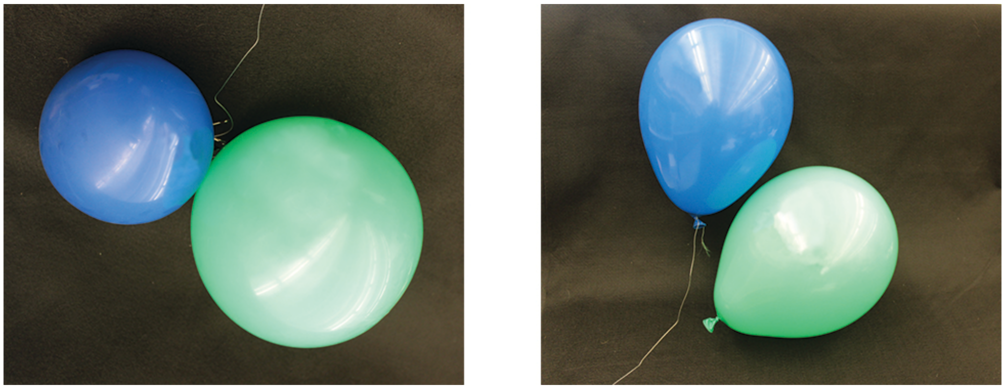

Figure 12.3c A balloon filled with air (the blue one) remains full overnight. A balloon filled with helium (the green one) partially deflates because the smaller, light helium atoms effuse through small holes in the rubber much more readily than the heavier molecules of nitrogen and oxygen found in air. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).)

Example 12.3a

Applying Graham's Law to Rates of Effusion

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{1.43\ \cancel{\text{g L}^{-1}}}}{\sqrt{0.0899\ \cancel{\text{g L}^{-1}}}} = \frac{1.20}{0.300} = \frac{4}{1}$$

Using molar masses:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{32\ \cancel{\text{g mol}}^{-1}}}{\sqrt{2\ \cancel{\text{mol L}}^{-1}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

Exercise 12.3a

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Using the same apparatus at the same temperature and pressure, at what rate will sulfur dioxide effuse?

Check Your Answer[1]

Here's another example, making the point about how determining times differs from determining rates.

Example 12.3b

Effusion Time Calculations

It takes 243 s for 4.46 × 10^{-5} mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take 4.46 × 10^{-5} mol Ne to effuse?

Solution

It is important to resist the temptation to use the times directly, and to remember how rate relates to time as well as how it relates to mass. Recall the definition of rate of effusion:

$$\text{rate of effusion} = \frac{\text{amount of gas transferred}}{\text{time}}$$

and combine it with Graham's law:

$$\frac{\text{rate of effusion of gas Xe}}{\text{rate of effusion of gas Ne}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

To get:

$$\frac{\frac{\text{amount of Xe transferred}}{\text{time for Xe}}}{\frac{\text{amount of Ne transferred}}{\text{time for Ne}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

Noting that *amount of A* = *amount of B*, and solving for *time for Ne*:

$$\frac{\frac{\cancel{\text{amount of Xe}}}{\text{time for Xe}}}{\frac{\cancel{\text{amount of Ne}}}{\text{time for Ne}}} = \frac{\text{time for Ne}}{\text{time for Xe}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

and substitute values:

$$\frac{\text{time for Ne}}{243\text{ s}} = \sqrt{\frac{20.2\ \cancel{\text{g mol}}}{131.3\ \cancel{\text{g mol}}}} = 0.392$$

Finally, solve for the desired quantity:

$$\text{time for Ne} = 0.392 \times 243\text{ s} = 95.3\text{ s}$$

Note that this answer is reasonable: Since Ne is lighter than Xe, the effusion rate for Ne will be larger than that for Xe, which means the time of effusion for Ne will be smaller than that for Xe.

Exercise 12.3b

A party balloon filled with helium deflates to $\frac{2}{3}$ of its original volume in 8.0 hours. How long will it take an identical balloon filled with the same number of moles of air ($\mathcal{M}$ = 28.2 g/mol) to deflate to $\frac{1}{2}$ of its original volume?

Check Your Answer[2]

Finally, here is one more example showing how to calculate molar mass from effusion rate data.

Example 12.3c

Determining Molar Mass Using Graham's Law

An unknown gas effuses 1.66 times more rapidly than CO_2. What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of Unknown}}{\text{rate of effusion of CO}_2} = \frac{\sqrt{\mathcal{M}_{\mathrm{CO_2}}}}{\sqrt{\mathcal{M}_{Unknown}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0\ \mathrm{g/mol}}}{\sqrt{\mathcal{M}_{Unknown}}}$$

Solve:

$$\mathcal{M}_{Unknown} = \frac{44.0\ \mathrm{g/mol}}{(1.66)^2} = 16.0\ \mathrm{g/mol}$$

The gas could well be CH_4, the only gas with this molar mass.

Exercise 12.3c

Hydrogen gas effuses through a porous container 8.97-times faster than an unknown gas. Estimate the molar mass of the unknown gas.

Check Your Answer[3]

Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of ^{235}U, the kind of uranium that is "fissile," that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5% ^{235}U, and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham's law. In a gaseous diffusion enrichment plant, uranium hexafluoride (UF_6, the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The $^{235}UF_6$ molecules have a higher average speed and diffuse through the barrier a little faster than the heavier $^{238}UF_6$ molecules. The gas that has passed through the barrier is slightly enriched in $^{235}UF_6$ and the residual gas is slightly depleted. The small difference in molecular weights between $^{235}UF_6$ and $^{238}UF_6$ only about 0.4% enrichment, is achieved in one diffuser (Figure 12.3d). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.

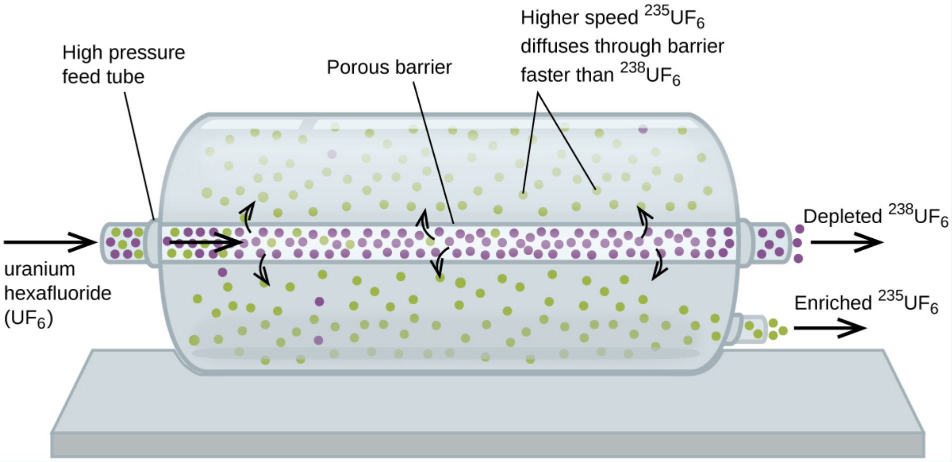

Figure 12.3d In a diffuser, gaseous UF_6 is pumped through a porous barrier, which partially separates $^{235}UF_6$ from $^{238}UF_6$ The UF_6 must pass through many large diffuser units to achieve sufficient enrichment in ^{235}U. (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The large scale separation of gaseous $^{235}UF_6$ from $^{238}UF_6$ was first done during the World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about 10^{-6} cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive UF_6.

Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now being replaced by gas centrifuge technology, which requires far less energy. A current hot political issue is how to deny this technology to Iran, to prevent it from producing enough enriched uranium for them to use to make nuclear weapons.

Key Equations

- $\text{rate of diffusion} = \dfrac{\text{amount of gas passing through an area}}{\text{unit of time}}$
- $\dfrac{\text{rate of effusion of gas A}}{\text{rate of effusion of gas B}} = \dfrac{\sqrt{m_B}}{\sqrt{m_A}} = \dfrac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}}$

Attribution & References

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Notes

1. 52 mL/s
2. 32 h
3. 163 g/mol

12.4 STOICHIOMETRY OF GASEOUS SUBSTANCES, MIXTURES, AND REACTIONS

Learning Objectives

By the end of this section, you will be able to:

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton’s law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behaviour of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the “father of modern chemistry,” changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, “It took the mob only a moment to remove his head; a century will not suffice to reproduce it.”[1]

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask “How much?” We can answer the question with masses of substances or volumes of solutions. However, we can also answer this question another way: with volumes of gases. We can use the ideal gas equation to relate the pressure, volume, temperature, and number of moles of a gas. Here we will combine the ideal gas equation with other equations to find gas density and molar mass. We will deal with mixtures of different gases, and calculate amounts of substances in reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

Density of a Gas

Recall that the density of a gas is its mass to volume ratio, $\rho = \frac{m}{V}$. Therefore, if we can determine the mass of some volume of a gas, we will get its density. The density of an unknown gas can be used to determine its molar mass and thereby assist in its identification. The ideal gas law, $PV = nRT$, provides us with a means of deriving such a mathematical formula to relate the density of a gas to its volume in the proof shown in Example 1.

Example 12.4a

Derivation of a Density Formula from the Ideal Gas Law

Use $PV = nRT$ to derive a formula for the density of gas in g/L

Solution

1. *$PV = nRT$*
2. *Rearrange to get (mol/L):* $\frac{n}{v} = \frac{P}{RT}$
3. *Multiply each side of the equation by the molar mass,* $\mathcal{M}$. When moles are multiplied by $\mathcal{M}$ in g/mol, g are obtained:
   $(\mathcal{M})(\frac{n}{V}) = (\frac{P}{RT})(\mathcal{M})$
4. $g/\mathrm{L} = \rho = \frac{P\mathcal{M}}{RT}$

Exercise 12.4a

A gas was found to have a density of 0.0847 g/L at 17.0 °C and a pressure of 760 torr. What is its molar mass? What is the gas?

Check Your Answer[2]

We must specify both the temperature and the pressure of a gas when calculating its density because the number of moles of a gas (and thus the mass of the gas) in a litre changes with temperature or pressure. Gas densities are often reported at STP.

Example 12.4b

Empirical/Molecular Formula Problems Using the Ideal Gas Law and Density of a Gas

Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

Strategy: First solve the empirical formula problem using methods discussed earlier. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen. In the last step, realize that the smallest whole number ratio is the empirical formula:

$$85.7\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g C}} = 7.136\text{ mol C} \qquad \frac{7.136}{7.136} = 1.00\text{ mol C}$$

$$14.3\text{ g H} \times \frac{1\text{ mol H}}{1.01\text{ g H}} = 14.158\text{ mol H} \qquad \frac{14.158}{7.136} = 1.98\text{ mol H}$$

Empirical formula is CH_2 [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the density equation related to the ideal gas law to determine the molar mass:

$$\text{d} = \frac{P\mathcal{M}}{RT} \quad \frac{1.56\text{ g}}{1.00\text{ L}} = 0.984\text{ atm} \times \frac{\mathcal{M}}{0.0821\text{ L atm/mol K}} \times 323\text{ K}$$

$\mathcal{M}$ = 42.0 g/mol, $\frac{\mathcal{M}}{\text{E}\mathcal{M}} = \frac{42.0}{14.03} = 2.99$, so (3)($CH_2$) = C_3H_6 (molecular formula)

Exercise 12.4b

Acetylene, a fuel used welding torches, is comprised of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Check Your Answer[3]

Molar Mass of a Gas

Another useful application of the ideal gas law involves the determination of molar mass. By definition, the molar mass of a substance is the ratio of its mass in grams, *m*, to its amount in moles, *n*:

$$\mathcal{M} = \frac{\text{grams of substance}}{\text{moles of substance}} = \frac{m}{n}$$

The ideal gas equation can be rearranged to isolate *n*:

$$n = \frac{PV}{RT}$$

and then combined with the molar mass equation to yield:

$$\mathcal{M} = \frac{mRT}{PV}$$

This equation can be used to derive the molar mass of a gas from measurements of its pressure, volume, temperature, and mass.

Example 12.4c

Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (see Figure 12.4a)

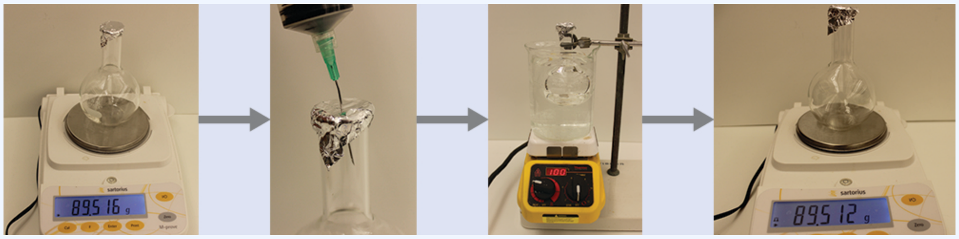


Figure 12.4a When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_{l \rightarrow g}$, the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since $\mathcal{M} = \frac{m}{n}$ and $n = \frac{PV}{RT}$, substituting and rearranging gives $\mathcal{M} = \frac{mRT}{PV}$,

then

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494 \text{ g}) \times 0.08206 \text{ L} \cdot \text{atm/mol K} \times 372.8 \text{ K}}{0.976 \text{ atm} \times \ 0.129 \text{ L}} = 120 \text{ g/mol}$$

Exercise 12.4c

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapour?

Check Your Answer[4]

The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure 12.4b). The pressure exerted by each individual gas in a mixture is called its **partial pressure**. This observation is summarized by **Dalton's law of partial pressures**: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{Total} = P_A + P_B + P_C + \cdots = \sum_{\mathrm{i}} P_{\mathrm{i}}$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_{A} is the partial pressure of gas A; P_{B} is the partial pressure of gas B; P_{C} is the partial pressure of gas C; and so on.

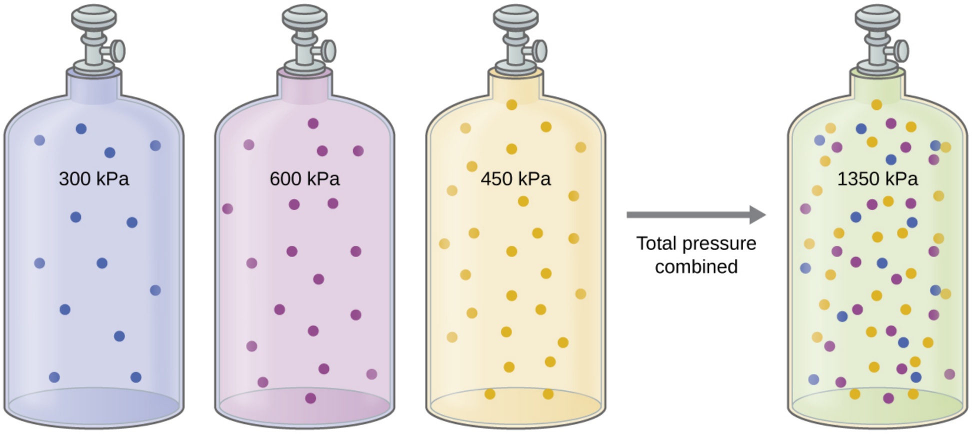


Figure 12.4b If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction (*X*)**, a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

Example 12.4d

The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50 × 10^{-3} mol of H_2, 1.00 × 10^{-3} mol of He, and 3.00 × 10^{-4} mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \dfrac{nRT}{V}$:

$$P_{\mathrm{H_2}} = \frac{(2.50 \times 10^{-3}\ \cancel{\mathrm{mol}})(0.08206\ \cancel{\mathrm{L}}\ \mathrm{atm}\ \cancel{\mathrm{mol}^{-1}}\cancel{\mathrm{K}^{-1}})(308\ \cancel{\mathrm{K}})}{10.0\ \cancel{\mathrm{L}}} = 6.32 \times 10^{-3}\ \mathrm{atm}$$

$$P_{\mathrm{He}} = \frac{(1.00 \times 10^{-3}\ \cancel{\mathrm{mol}})(0.08206\ \cancel{\mathrm{L}}\ \mathrm{atm}\ \cancel{\mathrm{mol}^{-1}}\cancel{\mathrm{K}^{-1}})(308\ \cancel{\mathrm{K}})}{10.0\ \cancel{\mathrm{L}}} = 2.53 \times 10^{-3}\ \mathrm{atm}$$

$$P_{\mathrm{Ne}} = \frac{(3.00 \times 10^{-4}\ \cancel{\mathrm{mol}})(0.08206\ \cancel{\mathrm{L}}\ \mathrm{atm}\ \cancel{\mathrm{mol}^{-1}}\cancel{\mathrm{K}^{-1}})(308\ \cancel{\mathrm{K}})}{10.0\ \cancel{\mathrm{L}}} = 7.58 \times 10^{-4}\ \mathrm{atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_{\mathrm{T}} = P_{\mathrm{H_2}} + P_{\mathrm{He}} + P_{\mathrm{Ne}} = (0.00632 + 0.00253 + 0.00076)\ \mathrm{atm} = 9.61 \times 10^{-3}\ \mathrm{atm}$$

Exercise 12.4d

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Check Your Answer[5]

Here is another example of this concept, but dealing with mole fraction calculations.

Example 12.4e

The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O_2, and 8.41 mol nitrous oxide, N_2O. The total pressure of the mixture is 192 kPa.

a. What are the mole fractions of O_2 and N_2O?
b. What are the partial pressures of O_2 and N_2O?

Solution

The mole fraction is given by $X_A = \frac{n_A}{n_{Total}}$ and the partial pressure is $P_A = X_A \times P_{Total}$.

For O_2,

$$X_{O_2} = \frac{n_{O_2}}{n_{Total}} = \frac{2.83 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.252$$

and $P_{O_2} = X_{O_2} \times P_{Total} = 0.252 \times 192 \text{ kPa} = 48.4 \text{ kPa}$

For N_2O,

$$X_{N_2} = \frac{n_{N_2}}{n_{Total}} = \frac{8.41 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.748$$

and

$$P_{N_2} = X_{N_2} \times P_{Total} = 0.748 \times 192 \text{ kPa} = 143.6 \text{ kPa}$$

Exercise 12.4e

What is the pressure of a mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Check Your Answer[6]

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 12.4c), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

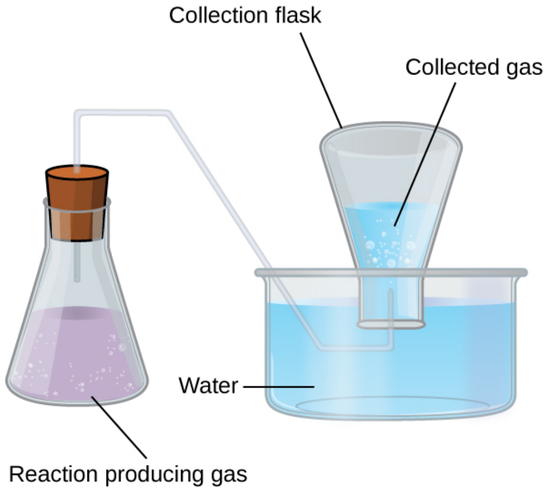


Figure 12.4c When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapour. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapour) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapour and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapour. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapour—this is referred to as the "dry" gas pressure, that is, the pressure of the gas only, without water vapour. The **vapour pressure of water**, which is the pressure exerted by water vapour in equilibrium with liquid water in a closed container, depends on the temperature (Figure 12.4d); more detailed information on the temperature dependence of water vapour can be found in Table 12.4a, and vapour pressure will be discussed in more detail in the next chapter on liquids.

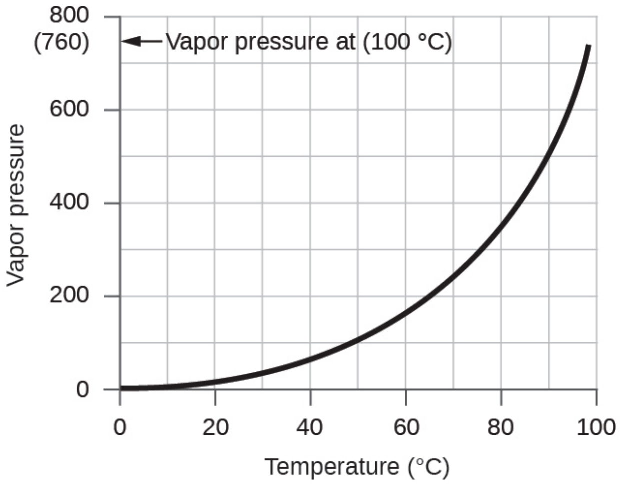


Figure 12.4d This graph shows the vapour pressure of water at sea level as a function of temperature (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Table 12.4a Vapour Pressure of Ice and Water in Various Temperatures at Sea Level

Temperatures -10 to 16 (°C)	Pressures at -10 to 16°C (torr)	Temperatures 18 to 29 (°C)	Pressures at 18 to 29°C (torr)	Temperatures 30 to 101.0 (°C)	Pressures at 30 to 101.0 °C (torr)
–10	1.95	18	15.5	30	31.8
–5	3.0	19	16.5	35	42.2
–2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

Example 12.4f

Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure 3, what is the partial pressure of argon?

Solution

According to Dalton's law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_{\mathrm{T}} = P_{\mathrm{Ar}} + P_{\mathrm{H_2O}}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{\mathrm{Ar}} = P_{\mathrm{T}} - P_{\mathrm{H_2O}}$$

The pressure of water vapour above a sample of liquid water at 26 °C is 25.2 torr (Appendix F), so:

$$P_{\mathrm{Ar}} = 750\ \mathrm{torr} - 25.2\ \mathrm{torr} = 725\ \mathrm{torr}$$

Exercise 12.4f

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

Check Your Answer[7]

Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions.

We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behaviour contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g)$, a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure 12.4e. According to Avogadro's law, equal volumes of gaseous N_2, H_2, and NH_3, at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3, the volume of H_2 required is three times the volume of N_2, and the volume of NH_3 produced is two times the volume of N_2.

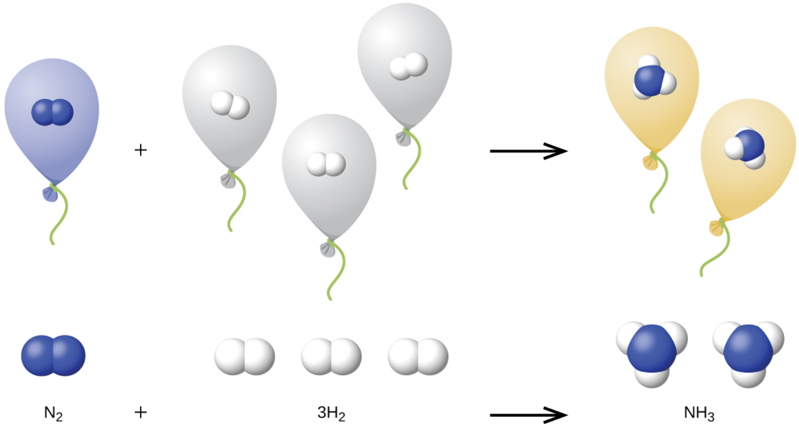


Figure 12.4e One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 12.4g

Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\begin{array}{ccc} C_3H_8(g) + 5O_2(g) & \longrightarrow & 3CO_2(g) + 4H_2O(l) \\ \\ 1\ \text{volume} + 5\ \text{volumes} & & 3\ \text{volumes} + 4\ \text{volumes} \end{array}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.7\ \cancel{\text{L C}_3\text{H}_8} \times \frac{5\ \text{L O}_2}{1\ \cancel{\text{L C}_3\text{H}_8}} = 13.5\ \text{L O}_2$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 12.4g

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2\text{C}_2\text{H}_2 + 5\text{O}_2 \longrightarrow 4\text{CO}_2 + 2\text{H}_2\text{O}$$

Check Your Answer[8]

Example 12.4h

Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683\ \cancel{\text{billion ft}^3\ \text{NH}_3} \times \frac{3\ \text{billion ft}^3\ \text{H}_2}{2\ \cancel{\text{billion ft}^3}\ \text{NH}_3} = 1.02 \times 10^3\ \text{billion ft}^3\ \text{H}_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

Exercise 12.4h

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapour.

Check Your Answer[9]

Example 12.4i

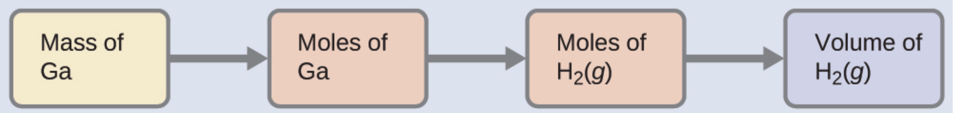
Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$2\text{Ga}(s) + 6\text{HCl}(aq) \longrightarrow 2\text{GaCl}_3(aq) + 3\text{H}_2(g)$$

Solution

To convert from the mass of gallium to the volume of $H_2(g)$, we need to do something like this:



The first two conversions are:

$$8.88\ \cancel{\text{g Ga}} \times \frac{1\ \cancel{\text{mol Ga}}}{69.723\ \cancel{\text{g Ga}}} \times \frac{3\ \text{mol H}_2}{2\ \cancel{\text{mol Ga}}} = 0.191\ \text{mol H}_2$$

Finally, we can use the ideal gas law:

$$V_{\text{H}_2} = \left(\frac{nRT}{P}\right)_{\text{H}_2} = \frac{0.191\ \cancel{\text{mol}} \times 0.08206\ \text{L}\ \cancel{\text{atm mol}^{-1}}\text{K}^{-1} \times 300\ \text{K}}{0.951\ \cancel{\text{atm}}} = 4.94\ \text{L}$$

Exercise 12.4i

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning l.00 kg of sulfur in oxygen?

Check Your Answer[10]

Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. However, most of this IR radiation is absorbed by certain substances in the atmosphere, known as greenhouse gases, which re-emit this energy in all directions, trapping some of the heat. This maintains favourable living conditions—without atmosphere, the average global average temperature of 14 °C (57 °F) would be about –19 °C (–2 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 12.4f).

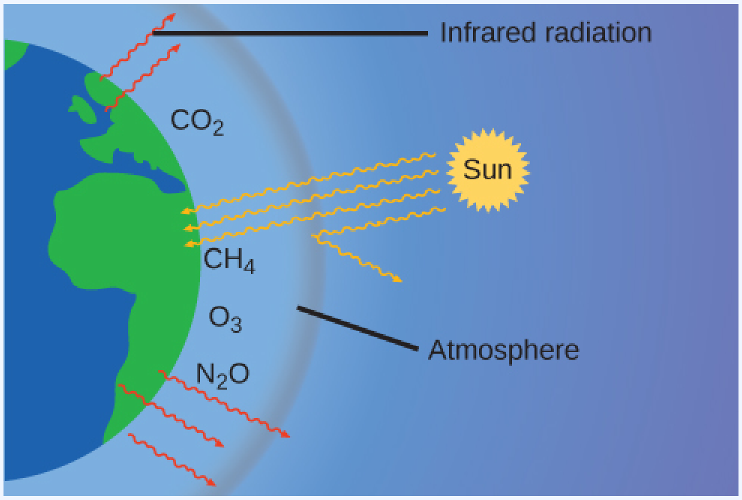


Figure 12.4f Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events (credit: *Chemistry (OpenStax)*, CC BY 4.0).

There is strong evidence from multiple sources that higher atmospheric levels of CO_2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO_2. Reliable data from ice cores reveals that CO_2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO_2 concentration has increased from historical levels of below 300 ppm to almost 400 ppm today.

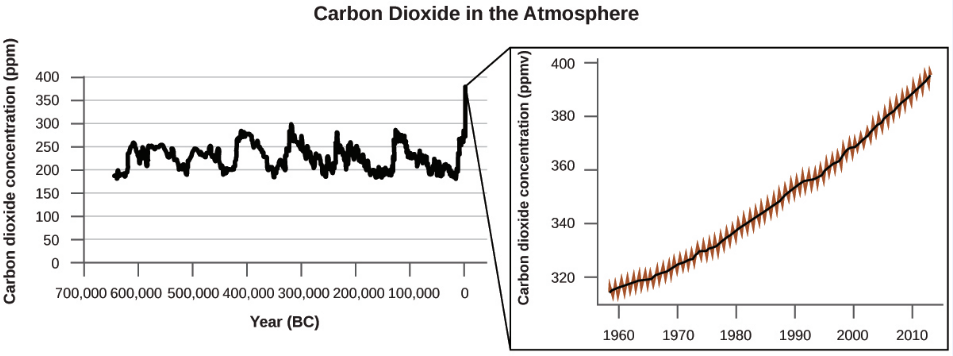


Figure 12.4g CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch The Greenhouse Effect (2 mins)

Scientists in Action: Dr. Susan Solomon

Figure 12.4h Atmospheric and climate scientist Susan Solomon (credit: work by Bengt Nyman, CC BY 2.0)

Atmospheric and climate scientist Dr. Susan Solomon (Figure 12.4h) is the author of one of *The New York Times* books of the year (*The Coldest March*, 2001), one of Time magazine's 100 most influential people in the world (2008), and a working group leader of the Intergovernmental Panel on Climate Change (IPCC), which was the recipient of the 2007 Nobel Peace Prize. She helped determine and explain the cause of the formation of the ozone hole over Antarctica, and has authored many important papers on climate change.

She has been awarded the top scientific honours in the US and France (the National Medal of Science and the Grande Medaille, respectively), and is a member of the National Academy of Sciences, the Royal Society, the French Academy of Sciences, and the European Academy of Sciences. Formerly a professor at the University of Colorado, she is now at MIT, and continues to work at NOAA.

For more information, watch Introducing: Atmospheric Chemist – Prof. Susan Solomon [New Tab]

Key Equations

- $P_{Total} = P_A + P_B + P_C + \cdots = \sum_{\mathrm{i}} P_{\mathrm{i}}$
- $P_A = X_A P_{Total}$
- $X_A = \dfrac{n_A}{n_{Total}}$

Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from "9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions" In *Chemistry 2e (OpenStax)* by Paul Flowers, Klaus Theopold, Richard Langley, & William R. Robinson, licensed under CC BY 4.0. Access for free at *Chemistry 2e (OpenStax)*.

Notes

1. “Quotations by Joseph-Louis Lagrange,” last modified February 2006, accessed February 10, 2015, http://www-history.mcs.st-andrews.ac.uk/Quotations/Lagrange.html
2. $\rho = \dfrac{P\mathcal{M}}{RT}$
   $0.0847\ \text{g/L} = 760\ \cancel{\text{torr}} \times \dfrac{1\ \cancel{\text{atm}}}{760\ \cancel{\text{torr}}} \times \dfrac{\mathcal{M}}{0.0821\ \text{L}\ \cancel{\text{atm}}/\text{mol K}} \times 290\ \text{K}$ $\mathcal{M}$ = 2.02 g/mol; therefore, the gas must be hydrogen (H_2, 2.02 g/mol)
3. Empirical formula, CH; Molecular formula, C_2H_2
4. 124 g/mol P_4
5. 1.137 atm
6. 1.87 atm
7. 0.583 L
8. 3.34 tanks (2.34 × 10^4 L)
9. 51.0 L
10. 1.30 × 10^3 L

12.5 THE KINETIC-MOLECULAR THEORY

Learning Objectives

By the end of this section, you will be able to:

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behaviour of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behaviour of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons', Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behaviour of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behaviour of a gas as follows:

- *Amonton's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure 12.5a.a).
- *Charles' law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas (Figure 12.5a.b).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure 12.5a.c).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

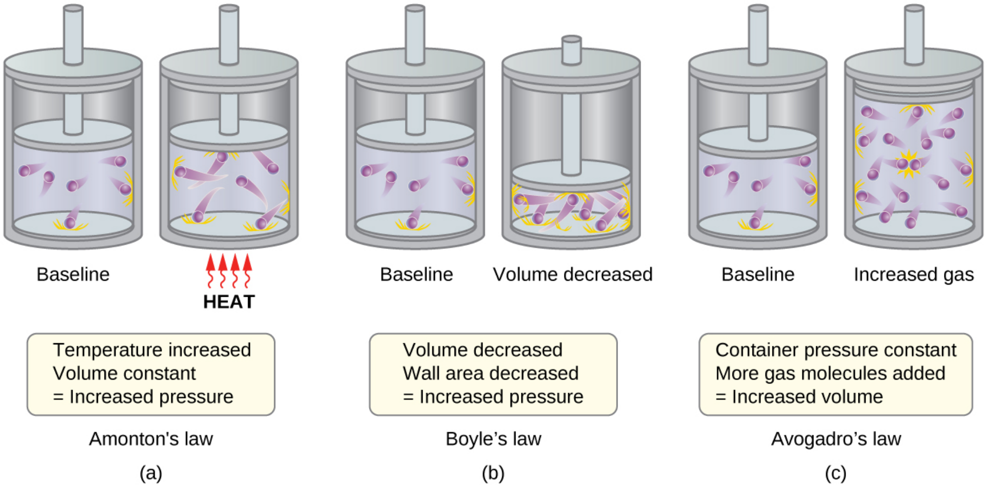


Figure 12.5a (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviours described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 12.5b).

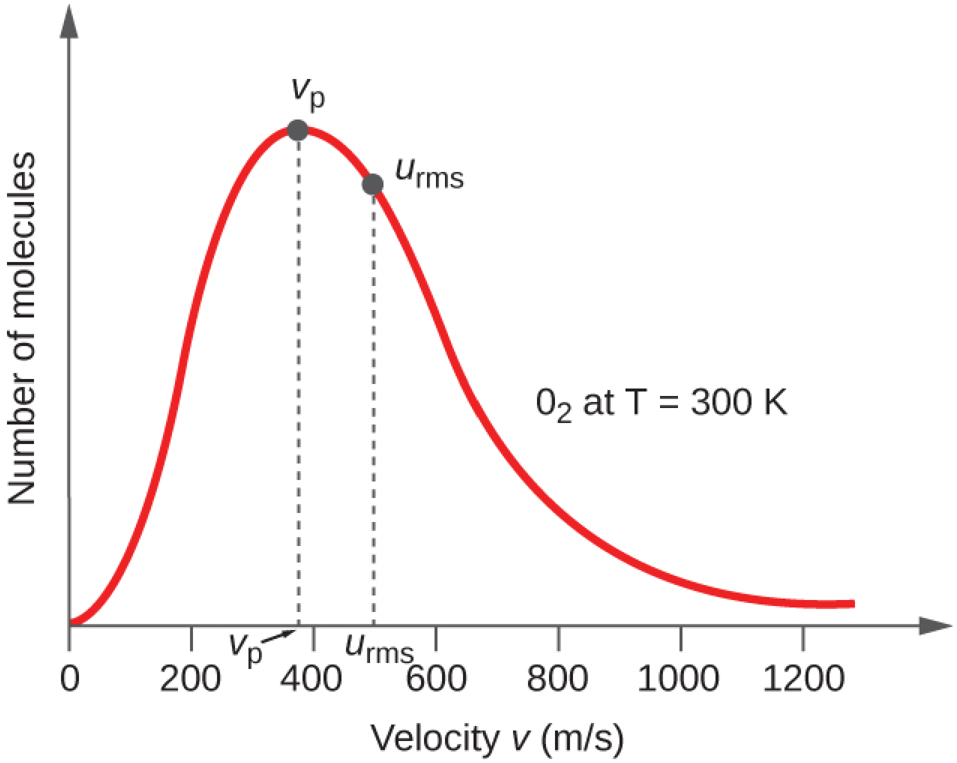


Figure 12.5b The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The kinetic energy (KE) of a particle of mass (*m*) and speed (*u*) is given by:

$$\text{KE} = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg $m^2 s^{-2}$). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the **root mean square velocity** of a particle, u_{rms}, is defined as the square root of the average of the squares of the velocities with *n* = the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \cdots}{n}}$$

The average kinetic energy, KE_{avg}, is then equal to:

$$\text{KE}_{\text{avg}} = \frac{1}{2}mu_{\text{rms}}^2$$

The KE_{avg} of a collection of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$\text{KE}_{\text{avg}} = \frac{3}{2}RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J/K (8.314 kg $\text{m}^2\text{s}^{-2}\text{K}^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2}mu_{\text{rms}}^2 = \frac{3}{2}RT$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

Example 12.5a

Calculation of u_{rms}

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30\ ^\circ\text{C} + 273 = 303\ \text{K}$$

Determine the mass of a nitrogen molecule in kilograms:

$$\frac{28.0\ \cancel{\text{g}}}{1\ \text{mol}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} = 0.028\ \text{kg/mol}$$

Replace the variables and constants in the root-mean-square velocity equation, replacing Joules with the equivalent kg m^2s^{-2}:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

$$u_{\text{rms}} = \sqrt{\frac{3(8.314\ \text{J/mol K})(303\ \text{K})}{(0.028\ \text{kg/mol})}} = \sqrt{2.70 \times 10^5\ \text{m}^2\text{s}^{-2}} = 519\ \text{m/s}$$

Exercise 12.5a

Calculate the root-mean-square velocity for an oxygen molecule at –23 °C.

Check Your Answer[1]

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behaviour is illustrated for nitrogen gas in Figure 12.5c.

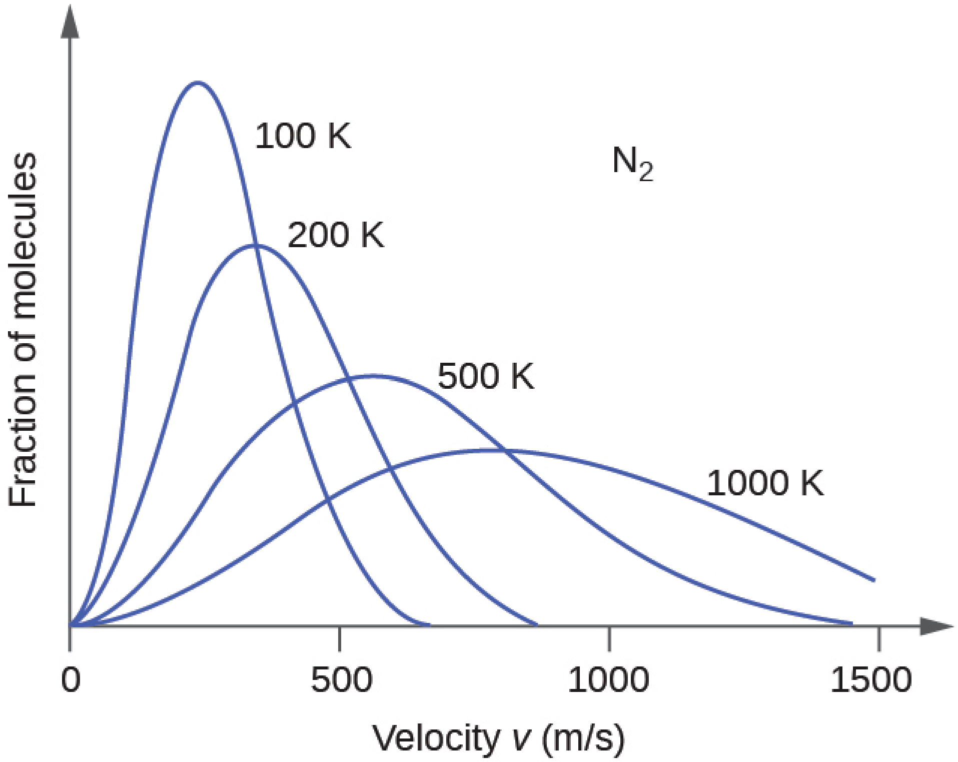


Figure 12.5c The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms}, with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in Figure 12.5d.

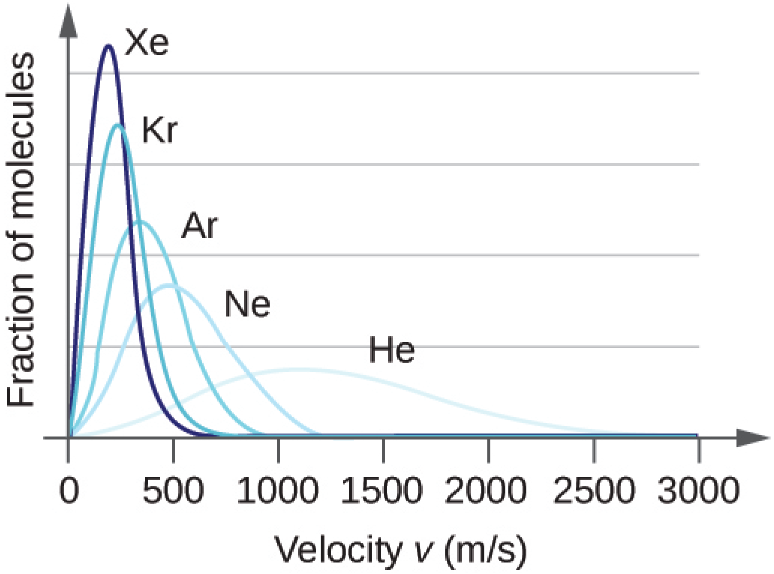


Figure 12.5d The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The simulator in Exercise 12.5b may be used to examine the effect of temperature on molecular velocities. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

Exercise 12.5b

Practice using the following PhET simulation: Gas Properties

The Kinetic-Molecular Theory Explains the Behaviour of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small.

The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion rate} \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

$$m = \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\overline{u}^2}$$

$$\frac{\text{effusion rate of A}}{\text{effusion rate of B}} = \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{m_{\text{A}}}}}{\sqrt{\frac{3RT}{m_{\text{B}}}}} = \sqrt{\frac{m_{\text{B}}}{m_{\text{A}}}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

Key Equations

- $u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\dfrac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \cdots}{n}}$
- $\text{KE}_{\text{avg}} = \dfrac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\dfrac{3RT}{m}}$

Attribution & References

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Notes

1. 441 m/s

12.6 NON-IDEAL GAS BEHAVIOUR

Learning Objectives

By the end of this section, you will be able to:

- Describe the physical factors that lead to deviations from ideal gas behaviour
- Explain how these factors are represented in the van der Waals equation
- Define compressibility (Z) and describe how its variation with pressure reflects non-ideal behaviour
- Quantify non-ideal behaviour by comparing computations of gas properties using the ideal gas law and the van der Waals equation

Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behaviour of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behaviour are considered.

One way in which the accuracy of $PV = nRT$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, V_m) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor (Z)** with:

$$\text{Z} = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT}\right)_\text{measured}$$

Ideal gas behaviour is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behaviour. Figure 12.6a shows plots of Z over a large pressure range for several common gases.

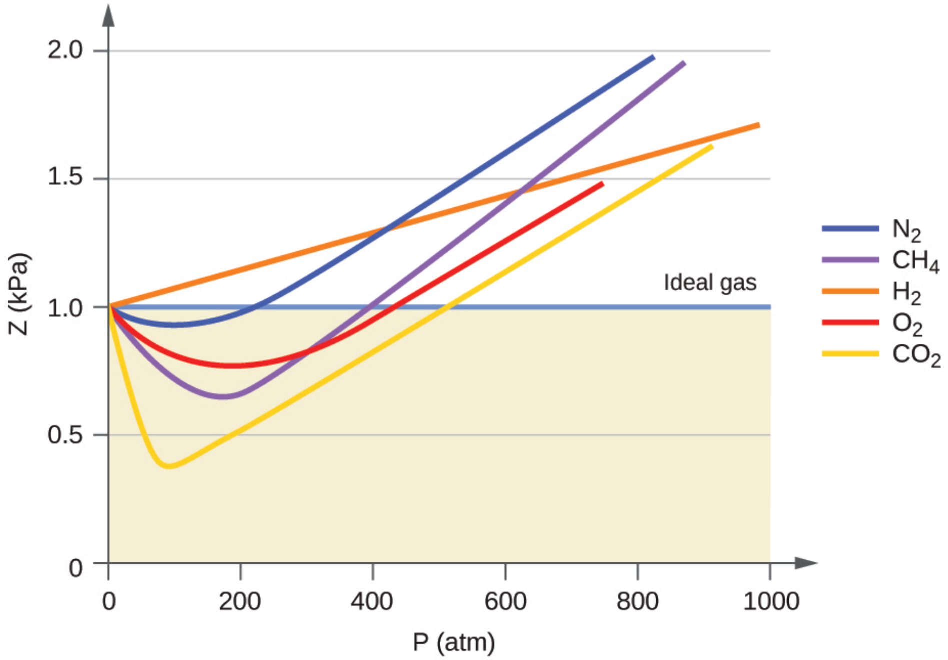

Figure 12.6a A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behaviour predicted by the ideal gas law (credit: *Chemistry (OpenStax)*, CC BY 4.0).

As is apparent from Figure 12.6a, the ideal gas law does not describe gas behaviour well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behaviour at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas (Figure 12.6b). The gas, therefore, becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 12.6b). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

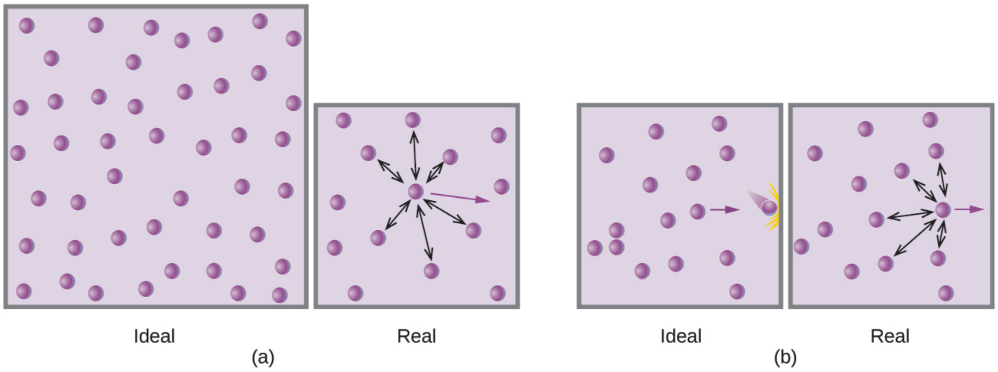

Figure 12.6b (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas (credit: *Chemistry (OpenStax)*, CC BY 4.0).

There are several different equations that better approximate gas behaviour than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

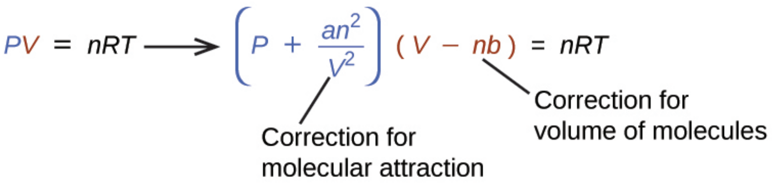

Figure 12.6c The van der Waals equation derived from the ideal gas law (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The constant *a* corresponds to the strength of the attraction between molecules of a particular gas, and the constant *b* corresponds to the size of the molecules of a particular gas. The "correction" to the pressure term in the ideal gas law is $\frac{n^2a}{V^2}$, and the "correction" to the volume is nb. Note that when V is relatively large and n is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, $PV = nRT$. Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in Table 12.6a.

Table 12.6a Values of van der Waals Constants for Some Common Gases

Gas	*a* (L^2 atm/mol^2)	*b* (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

At low pressures, the correction for intermolecular attraction, a, is more important than the one for molecular volume, b. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV = nRT$ over a small range of pressures. This behaviour is reflected by the "dips" in several of the compressibility curves shown in Figure 12.6a. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing P). At very high pressures, the gas becomes less compressible (Z increases with P), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Example 12.6a

Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO_2 at 229 °C. Calculate the pressure of this sample of CO_2:

a. from the ideal gas law
b. from the van der Waals equation
c. Explain the reason(s) for the difference.

Solution

a. From the ideal gas law: $P = \frac{nRT}{V} = \frac{3.46\ \cancel{\text{mol}} \times 0.08206\ \cancel{\text{L}}\ \text{atm}\ \cancel{\text{mol}}^{-1}\cancel{\text{K}}^{-1} \times 502\ \cancel{\text{K}}}{4.25\ \cancel{\text{L}}} = 33.5\ \text{atm}$

b. From the van der Waals equation:

$$(P + \frac{n^2a}{V^2}) \times (V - nb) = nRT \longrightarrow P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

$P = \frac{3.46\ \text{mol} \times 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 502\ \text{K}}{(4.25\ \text{L} - 3.46\ \text{mol} \times 0.0427\ \text{L mol}^{-1})} - \frac{(3.46\ \text{mol})^2 \times 3.59\text{L}^2\ \text{atm mol}^2}{(4.25\ \text{L})^2}$ This finally yields *P* = 32.4 atm.

c. This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO_2 molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

Exercise 12.6a

A 560-mL flask contains 21.3 g N_2 at 145 °C. Calculate the pressure of N_2:

a. from the ideal gas law
b. from the van der Waals equation
c. Explain the reason(s) for the difference.

Check Your Answer

1

Key Equations

- $Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = (\frac{P \times V_m}{R \times T})_{\text{measured}}$
- $(P + \frac{n^2a}{V^2}) \times (V - nb) = nRT$

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Notes

1. (a) 46.562 atm; (b) 46.594 atm; (c) The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

CHAPTER 12 - SUMMARY

12.1 Gas Pressure

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

12.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

The behaviour of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amonton's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles' law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant.

12.3 Effusion and Diffusion of Gases

Gaseous atoms and molecules move freely and randomly through space. Diffusion is the process whereby gaseous atoms and molecules are transferred from regions of relatively high concentration to regions of relatively low concentration. Effusion is a similar process in which gaseous species pass from a container to a vacuum through very small orifices. The rates of effusion of gases are inversely proportional to the square roots of their densities or to the square roots of their atoms/molecules' masses (Graham's law).

12.4 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses. Dalton's law of partial pressures may be used to relate measured gas pressures for gaseous mixtures to their compositions. Avogadro's law may be used in stoichiometric computations for chemical reactions involving gaseous reactants or products.

12.5 The Kinetic-Molecular Theory

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behaviour. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average speeds determined by their absolute temperatures. The individual molecules of a gas exhibit a range of speeds, the distribution of these speeds being dependent on the temperature of the gas and the mass of its molecules.

12.6 Non-Ideal Gas Behaviour

Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behaviour is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behaviour, and the gas is said to exhibit ideal behaviour. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behaviour of gases under these conditions.

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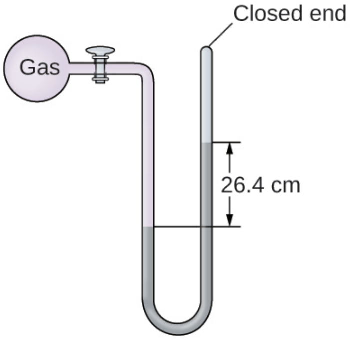
CHAPTER 12 - REVIEW

12.1 Gas Pressure

1. Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)? **Check Answer:** [1]
2. Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?
3. Why should you roll or belly-crawl rather than walk across a thinly-frozen pond? **Check Answer:** [2]
4. A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.
5. A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals? **Check Answer:** [3]
6. A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimetres of mercury, and in kilopascals?
7. Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi? **Check Answer:** [4]
8. During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?
9. The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi. **Check Answer:** [5]
10. A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?
11. Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in., 1013.9 mbar.
    1. What was the pressure in kPa?
    2. The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate the drop in pressure in torr.

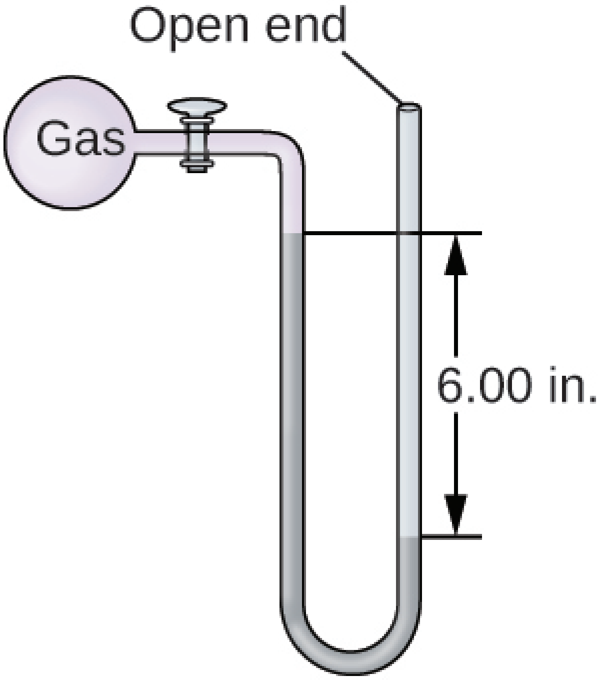
       Check Answer: [6]
12. Why is it necessary to use a nonvolatile liquid in a barometer or manometer?
13. The pressure of a sample of gas is measured at sea level with a closed-end manometer. See figure below. The liquid in the manometer is mercury. Determine the pressure of the gas in:

1. torr
2. Pa
3. bar

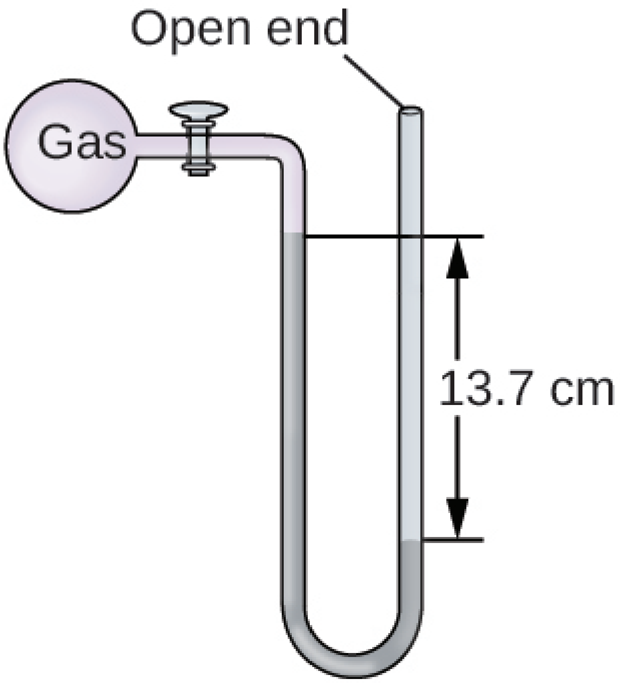


Check Answer: [7]

14. The pressure of a sample of gas is measured with an open-end manometer. See figure below. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:
    1. torr
    2. Pa



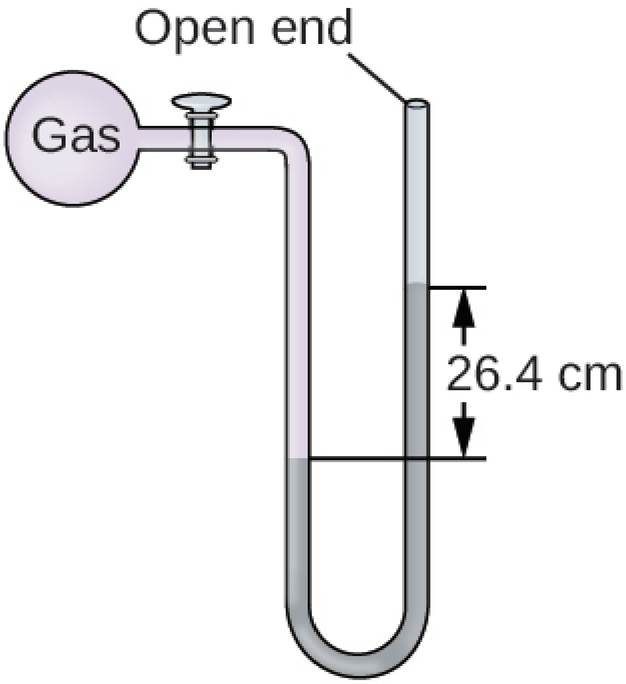
    3. bar
15. The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. See figure below. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:
    1. mm Hg
    2. atm



3. kPa

Check Answer: [8]

16. The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. See figure below. Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:
    1. mm Hg
    2. atm



    3. kPa
17. How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers vs. closed-end manometers? **Check Answer:** [9]

12.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

1. Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?
2. Explain how the volume of the bubbles exhausted by a scuba diver (Figure 12.2h) change as they rise to the surface, assuming that they remain intact. **Check Answer:** [10]
3. One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume." (a) What is the meaning of the term "inversely proportional?" (b) What are the "other things" that must be equal?
4. An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas." (a) What is the meaning of the term "directly proportional?" (b) What are the "other things" that must be equal? **Check Answer:** [11]
5. How would the graph in Figure 12.2d change if the number of moles of gas in the sample used to determine the curve were doubled?
6. How would the graph in Figure 12.2e change if the number of moles of gas in the sample used to determine the curve were doubled? **Check Answer:** [12]
7. In addition to the data found in Figure 12.2e , what other information do we need to find the mass of the sample of air used to determine the graph?
8. Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using Figure 12.2d **Check Answer:** [13]
9. Determine the pressure of the gas in the syringe shown in Figure 12.2e , when its volume is 12.5 mL, using:
   a. the appropriate graph
   b. Boyle's law
10. A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can? **Check Answer:** [14]
11. What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?
12. A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure. **Check Answer:** [15]
13. A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?
14. A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?

(credit: work by U.S. Department of Agriculture, CC BY 2.0)

Check Answer: [16]

15. The volume of an automobile air bag was 66.8 L when inflated at 25 °C with 77.8 g of nitrogen gas. What was the pressure in the bag in kPa?
16. How many moles of gaseous boron trifluoride, BF_3, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3? **Check Answer:** [17]
17. Iodine, I_2, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of I_2 vapour at a pressure of 0.462 atm?
18. How many grams of gas are present in each of the following cases?
    a. 0.100 L of CO_2 at 307 torr and 26 °C
    b. 8.75 L of C_2H_4, at 378.3 kPa and 483 K
    c. 221 mL of Ar at 0.23 torr and –54 °C
    Check Answer: [18]
19. A high altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21 °C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is –48 °C and the pressure is 63.1 torr?
20. A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C? **Check Answer:** [19]
21. A large scuba tank (Figure 12.2h) with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at 20 °C and contains enough air to supply 1860 L of air to a diver at a pressure of 2.37 atm (a depth of 45 feet). Was the tank filled to capacity at 20 °C?
22. A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the

mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C. **Check Answer:** [20]

23. While resting, the average 70-kg human male consumes 14 L of pure O_2 per hour at 25 °C and 100 kPa. How many moles of O_2 are consumed by a 70 kg man while resting for 1.0 h?
24. For a given amount of gas showing ideal behaviour, draw labeled graphs of:
    a. the variation of P with V
    b. the variation of V with T
    c. the variation of P with T
    d. the variation of $\frac{1}{P}$ with V

    Check Answer: [21]
25. A litre of methane gas, CH_4, at STP contains more atoms of hydrogen than does a litre of pure hydrogen gas, H_2, at STP. Using Avogadro's law as a starting point, explain why.
26. The effect of chlorofluorocarbons (such as CCl_2F_2) on the depletion of the ozone layer is well known. The use of substitutes, such as $CH_3CH_2F(g)$, for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:
    a. $CCl_2F_2(g)$
    b. $CH_3CH_2F(g)$

    Check Answer:
27. As 1 g of the radioactive element radium decays over 1 year, it produces 1.16×10^{18} alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?
28. A balloon that is 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?
    Check Answer: [22]
29. If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?
30. If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure? **Check Answer:** [23]

12.3 Effusion and Diffusion of Gases

1. A balloon filled with helium gas is found to take 6 hours to deflate to 50% of its original volume. How long will it take for an identical balloon filled with the same volume of hydrogen gas (instead of helium) to decrease its volume by 50%? **Check Answer:** [24]

2. Explain why the numbers of molecules are not identical in the left- and right-hand bulbs shown in the centre illustration of Figure 12.3a.
3. Starting with the definition of rate of effusion and Graham's finding relating rate and molar mass, show how to derive the Graham's law equation, relating the relative rates of effusion for two gases to their molecular masses. **Check Answer:** [25]
4. Heavy water, D_2O (molar mass = 20.03 g mol^{-1}), can be separated from ordinary water, H_2O (molar mass = 18.01), as a result of the difference in the relative rates of diffusion of the molecules in the gas phase. Calculate the relative rates of diffusion of H_2O and D_2O.
5. Which of the following gases diffuse more slowly than oxygen? F_2, Ne, N_2O, C_2H_2, NO, Cl_2, H_2S **Check Answer:** [26]
6. During the discussion of gaseous diffusion for enriching uranium, it was claimed that $^{235}UF_6$ diffuses 0.4% faster than $^{238}UF_6$. Show the calculation that supports this value. The molar mass of $^{235}UF_6$ = 235.043930 + 6 × 18.998403 = 349.034348 g/mol, and the molar mass of $^{238}UF_6$ = 238.050788 + 6 × 18.998403 = 352.041206 g/mol.
7. Calculate the relative rate of diffusion of $^1H_2$ (molar mass 2.0 g/mol) compared to that of $^2H_2$ (molar mass 4.0 g/mol) and the relative rate of diffusion of O_2 (molar mass 32 g/mol) compared to that of O_3 (molar mass 48 g/mol). **Check Answer:** [27]
8. A gas of unknown identity diffuses at a rate of 83.3 mL/s in a diffusion apparatus in which carbon dioxide diffuses at the rate of 102 mL/s. Calculate the molecular mass of the unknown gas.
9. When two cotton plugs, one moistened with ammonia and the other with hydrochloric acid, are simultaneously inserted into opposite ends of a glass tube that is 87.0 cm long, a white ring of NH_4Cl forms where gaseous NH_3 and gaseous HCl first come into contact. (Hint: Calculate the rates of diffusion for both NH_3 and HCl, and find out how much faster NH_3 diffuses than HCl.)
   $$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$
   At approximately what distance from the ammonia moistened plug does this occur? **Check Answer:** [28]

12.4 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

1. What is the density of laughing gas, dinitrogen monoxide, N_2O, at a temperature of 325 K and a pressure of 113.0 kPa?
2. Calculate the density of Freon 12, CF_2Cl_2, at 30.0 °C and 0.954 atm. **Check Answer:** [29]
3. Which is denser at the same temperature and pressure, dry air or air saturated with water vapour? Explain.
4. A cylinder of $O_2(g)$ used in breathing by emphysema patients has a volume of 3.00 L at a pressure of 10.0 atm. If the temperature of the cylinder is 28.0 °C, what mass of oxygen is in the cylinder? **Check**

Answer: [30]

5. What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?
6. What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 torr? **Check Answer:** [31]
7. How could you show experimentally that the molecular formula of propene is C_3H_6, not CH_2?
8. The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at STP. Calculate the molar mass of this fluoride and determine its molecular formula. **Check Answer:** [32]
9. Consider this question: What is the molecular formula of a compound that contains 39% C, 45% N, and 16% H if 0.157 g of the compound occupies l25 mL with a pressure of 99.5 kPa at 22 °C?
   a. Outline the steps necessary to answer the question.
   b. Answer the question.
10. A 36.0–L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g CO_2, 805 g O_2, and 4,880 g N_2. At 25 degrees C, what is the pressure in the cylinder in atmospheres? **Check Answer:** [33]
11. A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO_2, 12.0% O_2, and the remainder N_2 at a total pressure of 146 atm. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)
12. A sample of gas isolated from unrefined petroleum contains 90.0% CH_4, 8.9% C_2H_6, and 1.1% C_3H_8 at a total pressure of 307.2 kPa. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.) **Check Answer:** [34]
13. A mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar is stored in a closed container at STP. Find the volume of the container, assuming that the gases exhibit ideal behaviour.
14. Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O_2 is not. If enough O_2 is added to a cylinder of H_2 at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive? **Check Answer:** [35]
15. A commercial mercury vapour analyzer can detect, in air, concentrations of gaseous Hg atoms (which are poisonous) as low as 2×10^{-6} mg/L of air. At this concentration, what is the partial pressure of gaseous mercury if the atmospheric pressure is 733 torr at 26 °C?
16. A sample of carbon monoxide was collected over water at a total pressure of 756 torr and a temperature of 18 °C. What is the pressure of the carbon monoxide? (See Table 12.4a for the vapour pressure of water.) **Check Answer:** [36]
17. In an experiment in a general chemistry laboratory, a student collected a sample of a gas over water. The volume of the gas was 265 mL at a pressure of 753 torr and a temperature of 27 °C. The mass of the gas was 0.472 g. What was the molar mass of the gas?

18. Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:

    $$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$$

    a. Outline the steps necessary to answer the following question: What volume of O_2 at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?
    b. Answer the question.

    Check Answer: [37]

19. Cavendish prepared hydrogen in 1766 by the novel method of passing steam through a red-hot gun barrel:

    $$4\text{H}_2\text{O}(g) + 3\text{Fe}(s) \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2(g)$$

    1. Outline the steps necessary to answer the following question: What volume of H_2 at a pressure of 745 torr and a temperature of 20 °C can be prepared from the reaction of 15.O g of H_2O?
    2. Answer the question.

20. The chlorofluorocarbon CCl_2F_2 can be recycled into a different compound by reaction with hydrogen to produce $CH_2F_2(g)$, a compound useful in chemical manufacturing:

    $$\text{CCl}_2\text{F}_2(g) + 4\text{H}_2(g) \longrightarrow \text{CH}_2\text{F}_2(g) + 2\text{HCl}(g)$$

    a. Outline the steps necessary to answer the following question: What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton (1.000×10^3 kg) of CCl_2F_2?
    b. Answer the question.

    Check Answer: [38]

21. Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide (NaN_3). The other product is sodium metal. Calculate the volume of nitrogen gas at 27 °C and 756 torr formed by the decomposition of 125 g of sodium azide.

22. Lime, CaO, is produced by heating calcium carbonate, $CaCO_3$; carbon dioxide is the other product.

    a. Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875° and 0.966 atm is produced by the decomposition of 1 ton (1.000×10^3 kg) of calcium carbonate?
    b. Answer the question.

    Check Answer: [39]

23. Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas, C_2H_2, and solid calcium hydroxide were formed by the reaction of calcium carbide, CaC_2, with water. The ignition of the acetylene gas provided the light. Currently, the same lamps are used by some cavers, and calcium carbide is used to produce acetylene for carbide cannons.

    a. Outline the steps necessary to answer the following question: What volume of C_2H_2 at 1.005 atm and 12.2 °C is formed by the reaction of 15.48 g of CaC_2 with water?
    b. Answer the question.

24. Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C_2H_6, to produce carbon dioxide and water, if the volumes of C_2H_6 and O_2 are measured under the same conditions of

temperature and pressure. **Check Answer:** [40]

25. What volume of O_2 at STP is required to oxidize 8.0 L of NO at STP to NO_2? What volume of NO_2 is produced at STP?
26. Consider the following questions:
    a. What is the total volume of the $CO_2(g)$ and $H_2O(g)$ at 600 °C and 0.888 atm produced by the combustion of 1.00 L of $C_2H_6(g)$ measured at STP?
    b. What is the partial pressure of H_2O in the product gases? **Check Answer:** [41]
27. Methanol, CH_3OH, is produced industrially by the following reaction:

    $$\mathrm{CO}(g) + 2\mathrm{H}_2(g) \xrightarrow{\text{copper catalyst 300 °C, 300 atm}} \mathrm{CH_3OH}(g)$$

    Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.
28. What volume of oxygen at 423.0 K and a pressure of 127.4 kPa is produced by the decomposition of 129.7 g of BaO_2 to BaO and O_2? **Check Answer:** [42]
29. A 2.50-L sample of a colourless gas at STP decomposed to give 2.50 L of N_2 and 1.25 L of O_2 at STP. What is the colourless gas?
30. Ethanol, C_2H_5OH, is produced industrially from ethylene, C_2H_4, by the following sequence of reactions:

    $$3\mathrm{C_2H_4} + 2\mathrm{H_2SO_4} \longrightarrow \mathrm{C_2H_5HSO_4} + (\mathrm{C_2H_5})_2\mathrm{SO_4}$$
    $$\mathrm{C_2H_5HSO_4} + (\mathrm{C_2H_5})_2\mathrm{SO_4} + 3\mathrm{H_2O} \longrightarrow 3\mathrm{C_2H_5OH} + 2\mathrm{H_2SO_4}$$

    What volume of ethylene at STP is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%? **Check Answer:** [43]
31. One molecule of hemoglobin will combine with four molecules of oxygen. If 1.0 g of hemoglobin combines with 1.53 mL of oxygen at body temperature (37 °C) and a pressure of 743 torr, what is the molar mass of hemoglobin?
32. A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 torr. Hydrogen was added to the bulb until the pressure was 72 torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.) **Check Answer:** [44]
33. One method of analyzing amino acids is the van Slyke method. The characteristic amino groups ($-NH_2$) in protein material are allowed to react with nitrous acid, HNO_2, to form N_2 gas. From the volume of the gas, the amount of amino acid can be determined. A 0.0604-g sample of a biological sample containing glycine, $CH_2(NH_2)COOH$, was analyzed by the van Slyke method and yielded 3.70 mL of N_2 collected over water at a pressure of 735 torr and 29 °C. What was the percentage of glycine in the sample?

    $$\mathrm{CH_2\ (NH_2)CO_2H} + \mathrm{HNO_2} \longrightarrow \mathrm{CH_2\ (OH)CO_2H} + \mathrm{H_2O} + \mathrm{N_2}$$

12.5 The Kinetic-Molecular Theory

1. Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.
2. Can the speed of a given molecule in a gas double at constant temperature? Explain your answer. **Check Answer:** [45]
3. Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:
    a. The pressure of the gas is increased by reducing the volume at constant temperature.
    b. The pressure of the gas is increased by increasing the temperature at constant volume.
    c. The average velocity of the molecules is increased by a factor of 2.
4. The distribution of molecular velocities in a sample of helium is shown in Figure 12.5d. If the sample is cooled, will the distribution of velocities look more like that of H_2 or of H_2O? Explain your answer. **Check Answer:** [46]
5. What is the ratio of the average kinetic energy of a SO_2 molecule to that of an O_2 molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms}, of the two gases?
6. A 1-L sample of CO initially at STP is heated to 546 °C, and its volume is increased to 2 L.
    a. What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?
    b. What is the effect on the average kinetic energy of the molecules?
    c. What is the effect on the root mean square speed of the molecules?
    Check Answer: [47]
7. The root mean square speed of H_2 molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N_2 molecule at 25 °C?
8. Answer the following questions:
    a. Is the pressure of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
    b. Is the density of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
    c. At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?
    d. The average temperature of the gas in a hot air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.
    e. The lifting capacity of a hot air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?
    f. An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft^3. What is the lifting

power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?

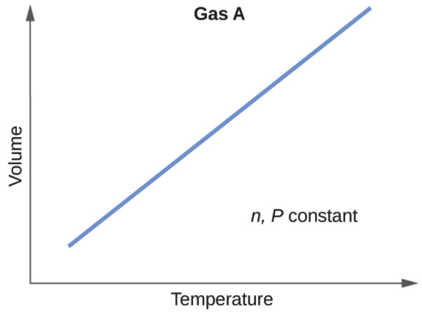
g. A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO_2 and H_2O gas is produced by the combustion of this propane?

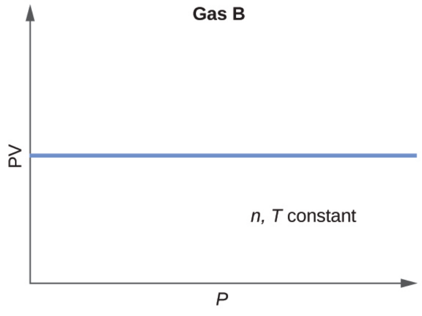
h. A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?
Check Answer: [48]

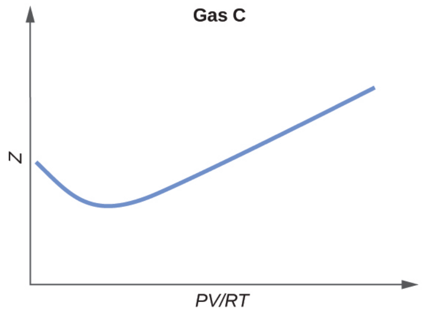
9. Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $\dfrac{R_1}{R_2}$, is the same at 0 °C and 100 °C.

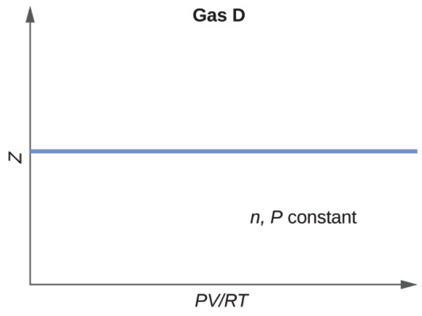
12.6 Non-Ideal Gas Behaviour

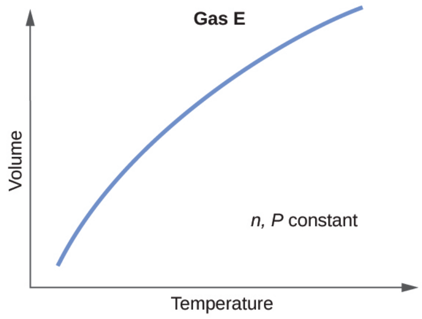
1. Graphs showing the behaviour of several different gases are below. Which of these gases exhibit behaviour significantly different from that expected for ideal gases?

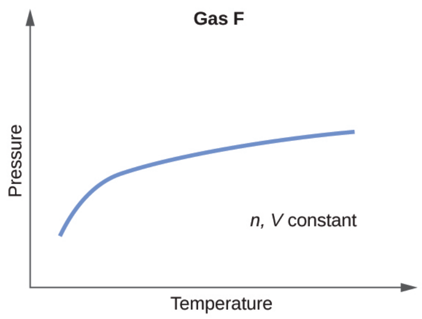






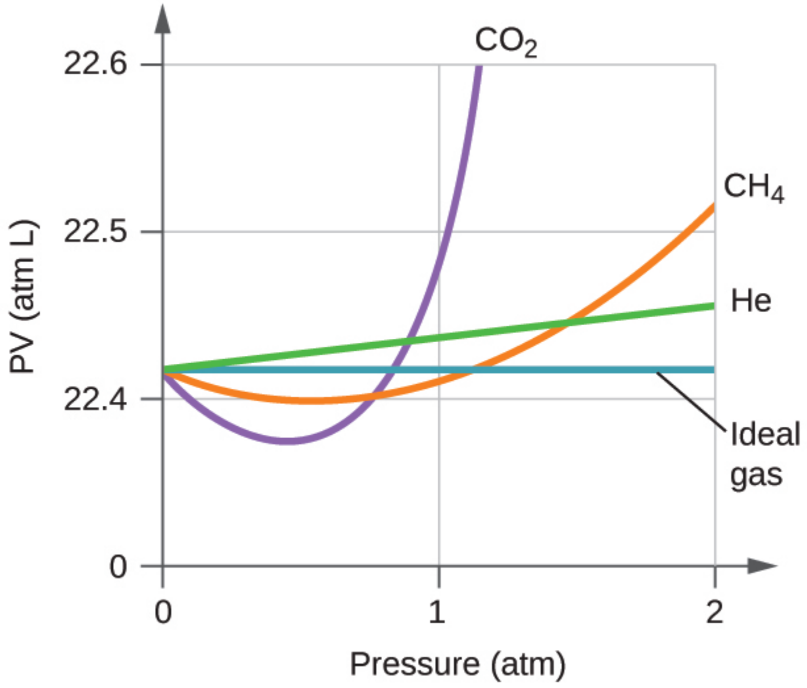






Check Answer: [49]

2. Explain why the plot of *PV* for CO_2 differs from that of an ideal gas. See figure below.



3. Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behaviour? Explain.
   1. high pressure, small volume
   2. high temperature, low pressure
   3. low temperature, high pressure

   Check Answer: [50]
4. Describe the factors responsible for the deviation of the behaviour of real gases from that of an ideal gas.
5. For which of the following gases should the correction for the molecular volume be largest: CO, CO_2, H_2, He, NH_3, SF_6? **Check Answer:** [51]
6. A 0.245-L flask contains 0.467 mol CO_2 at 159 °C. Calculate the pressure:
   1. using the ideal gas law
   2. using the van der Waals equation
   3. Explain the reason for the difference.
   4. Identify which correction (that for P or V) is dominant and why.
7. Answer the following questions:
   1. If XX behaved as an ideal gas, what would its graph of Z vs. P look like?
   2. For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
   3. What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
   4. What is the effect of intermolecular attractions on the value of Z? Under what conditions is this

effect small? When is it large? Explain using an appropriate diagram.

5. In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?
   Check Answer: [52]

Attribution & References

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- "8.1 Gas Pressure", "8.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law", "8.5 The Kinetic-Molecular Theory" and "8.6 Non-Ideal Gas Behavior" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*
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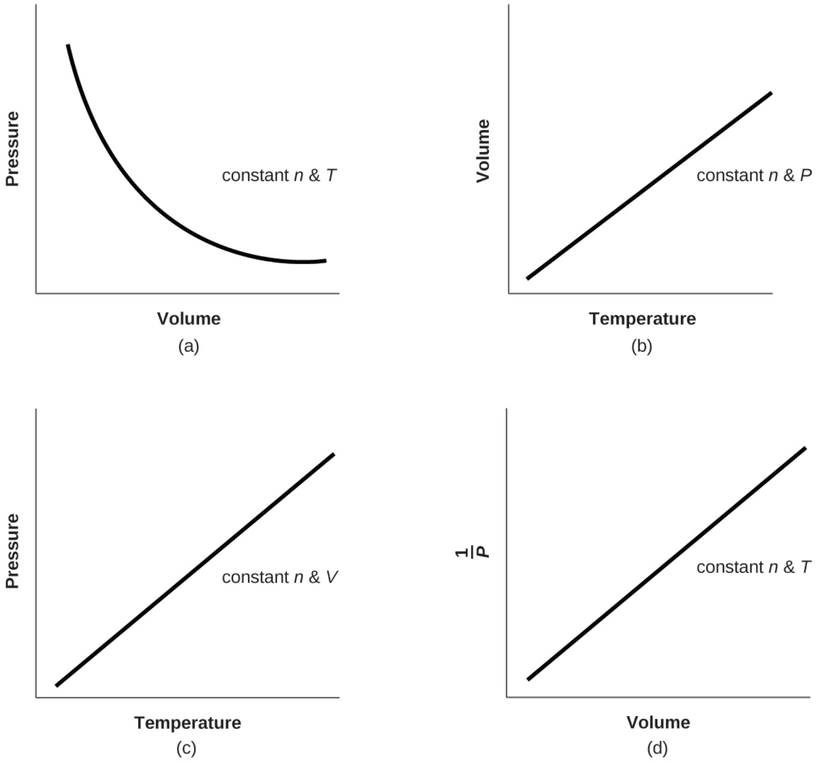
Notes

1. The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.
2. Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.
3. 0.809 atm; 82.0 kPa
4. 2.2×10^2 kPa
5. Earth: 14.7 lb in^{-2}; Venus: 13.1×10^3 lb in^{-2}
6. (a) 101.5 kPa; (b) 51 torr drop
7. (a) 264 torr; (b) 35,200 Pa; (c) 0.352 bar
8. (a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa
9. With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since $P_{\text{gas}} = P_{\text{atm}} + P_{\text{vol liquid}}$.
10. As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.
11. (a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure
12. The curve would be farther to the right and higher up, but the same basic shape.
13. 16.3 to 16.5 L
14. 3.40×10^3 torr

15. 12.1 L
16. 217 L
17. 8.190×10^{-2} mol; 5.553 g
18. (a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g
19. 5561 L
20. 46.4 g
21. For a gas exhibiting ideal behaviour:



22. 0.644 atm
23. The pressure decreases by a factor of 3.
24. 4.2 hours
25. Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B: $\left(\frac{\text{rate A}}{\text{rate B}}\right) = \left(\frac{\text{molar mass of B}}{\text{molar mass of A}}\right)^{1/2}$. Both A and B are in the same container at the same temperature, and therefore will have the same kinetic energy:

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A}$$

$$\mathrm{KE_A} = \mathrm{KE_B} \, \mathrm{KE} = \frac{1}{2}\, mv^2 \text{ Therefore, } \frac{1}{2} m_A {v^2}_A = \frac{1}{2} m_B {v^2}_B \left(\frac{v_A^2}{v_B^2}\right)^{1/2} = \left(\frac{m_B}{m_A}\right)^{1/2}$$

$$\left(\frac{v_A}{v_B}\right) = \left(\frac{m_B}{m_A}\right)^{1/2}$$

26. F_2, N_2O, Cl_2, H_2S

27. 1.4; 1.2
28. 51.7 cm
29. 4.64 g L^{-1}
30. 38.8 g
31. 72.0 g mol^{-1}
32. 88.1 g mol^{-1}; PF_3
33. 141 atm
34. CH_4: 276 kPa; C_2H_6: 27 kPa; C_3H_8: 3.4 kPa
35. Yes
36. 740 torr
37. (a) Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O_2 produced by decomposition of this amount of HgO; and determine the volume of O_2 from the moles of O_2, temperature, and pressure. (b) 0.308 L
38. (a) Determine the molar mass of CCl_2F_2. From the balanced equation, calculate the moles of H_2 needed for the complete reaction. From the ideal gas law, convert moles of H_2 into volume. (b) 3.72×10^3 L
39. (a) Balance the equation. Determine the grams of CO_2 produced and the number of moles. From the ideal gas law, determine the volume of gas. (b) 7.43×10^5 L
40. 42.00 L
41. (a) 18.0 L; (b) 0.533 atm
42. 10.57 L O_2
43. 5.40×10^5 L
44. XeF_2
45. Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.
46. H_2O. Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.
47. (a) The number of collisions per unit area of the container wall is constant. (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\sqrt{KE_{avg}}$.
48. (a) equal; (b) less than; (c) 29.48 g mol^{-1}; (d) 1.0966 g L^{-1}; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min^{-1}
49. Gases C, E, and F
50. The gas behaviour most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.
51. SF_6
52. (a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see Figure 12.6a) (d) Once again, at low pressures, the effect of intermolecular

attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See Figure 12.6a. (e) low temperatures

CHAPTER 13: PROPERTIES OF LIQUIDS AND WATER

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The types of intermolecular forces possible between atoms/molecules and within atoms/molecules, based on their structure and makeup
- The difference between adhesive and cohesive forces, and how these forces affect viscosity,

surface tension, and capillary rise
- Phase transitions and phase transition temperatures, and how intermolecular forces and kinetic energy affect these phenomena
- The processes represented by heating and cooling curves, and the enthalpy changes accompanying these processes
- The special characteristics of water, and how its structure gives it these unique properties

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- The difference between a physical and a chemical property of matter
- Enthalpy, and its classification as a state function
- Atomic properties and periodic table trends
- Molecular structure, as determined by VSEPR theory, and polarity of molecular bonds

Figure 13a Solid carbon dioxide ("dry ice", left) sublimes vigorously when placed in a liquid (right), cooling the liquid and generating a fog of condensed water vapour above the cylinder. (credit: modification of work by Paul Flowers in *Chemistry (OpenStax)*, CC BY 4.0).

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid state, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of the liquid phase will be examined.

Attribution & References

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13.1 INTERMOLECULAR FORCES

Learning Objectives

By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behaviour of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase “intermolecular attraction” to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles’ KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 13.1a illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

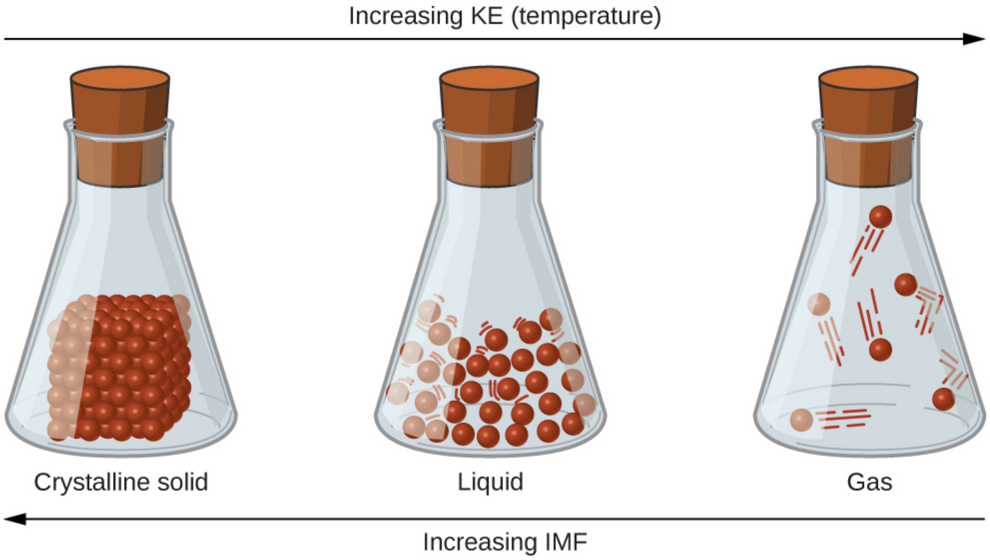

Figure 13.1a Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favour the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold window as the water vapour in the air is cooled by the cold glass, as seen in Figure 13.1b.

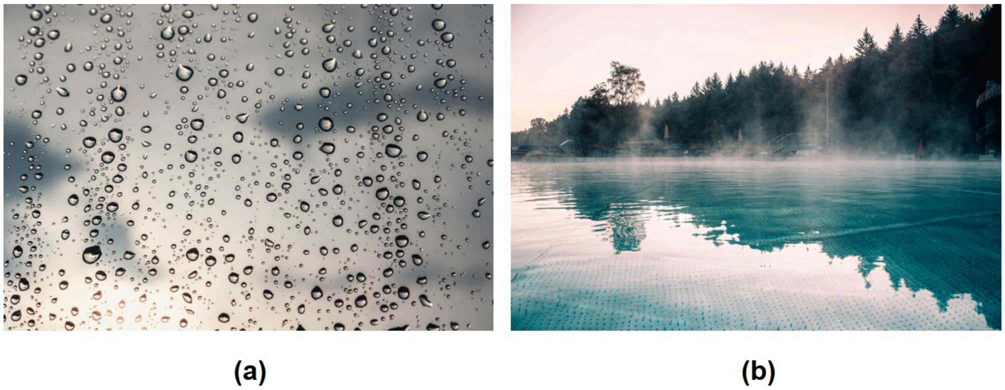

Figure 13.1b Condensation forms when water vapour in the air is cooled enough to form liquid water, such as (a) on the outside of a window or (b) in the form of fog. (credit a: work by Christian Wiediger, Unsplash license; credit b: work by Mary Noe, Unsplash license)

We can also liquefy many gases by compressing them if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 13.1c.

Figure 13.1c Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by Sam-Cat, CC BY 2.0)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Exercise 13.1a

Practice using the following PhET simulation: States of Matter

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 13.1d illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

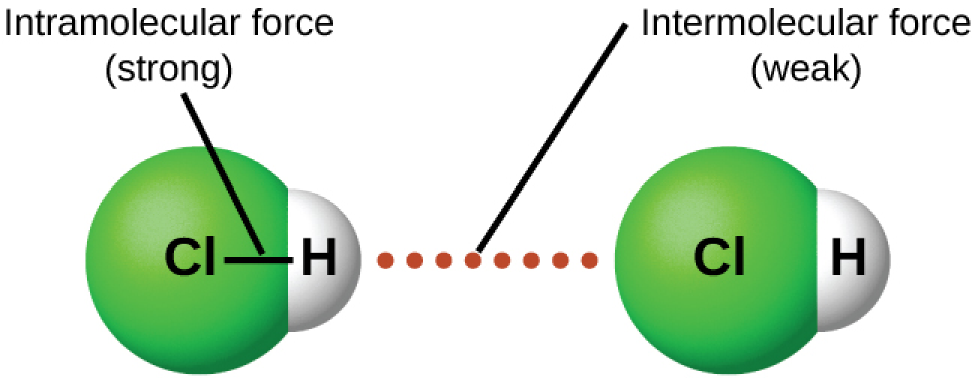

Figure 13.1d *Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties (credit: *Chemistry (OpenStax)*, CC BY 4.0).

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the **London dispersion force** in honour of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighbouring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 13.1e.

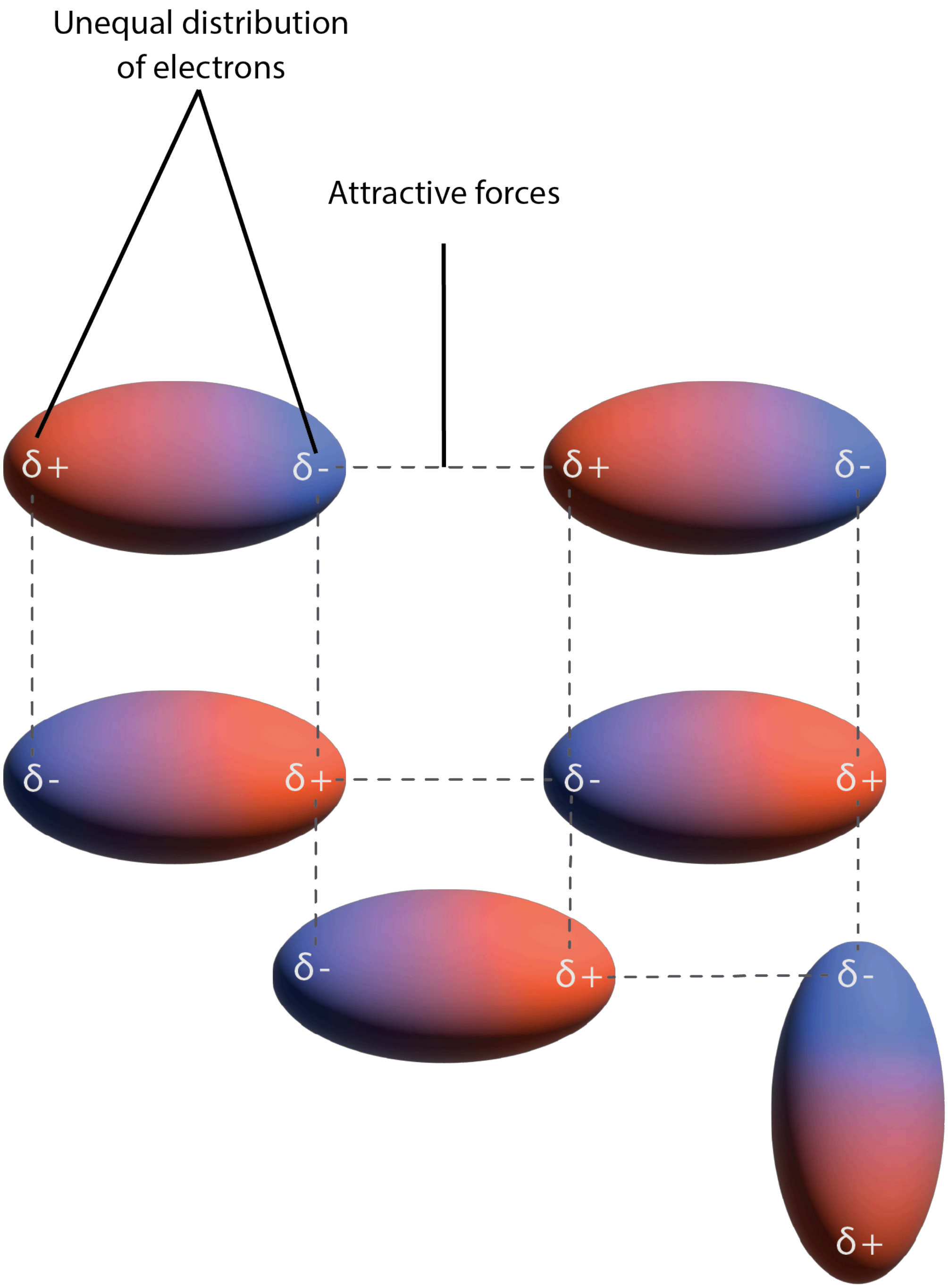

Figure 13.1e Dispersion forces result from the formation of temporary dipoles, as illustrated here for several nonpolar diatomic molecules (credit: graphic by Revathi Mahadevan, CC BY 4.0)

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 13.1a.

Table 13.1a Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 13.1a

London Forces and Their Effects

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 < SiH_4 < GeH_4 < SnH_4$.

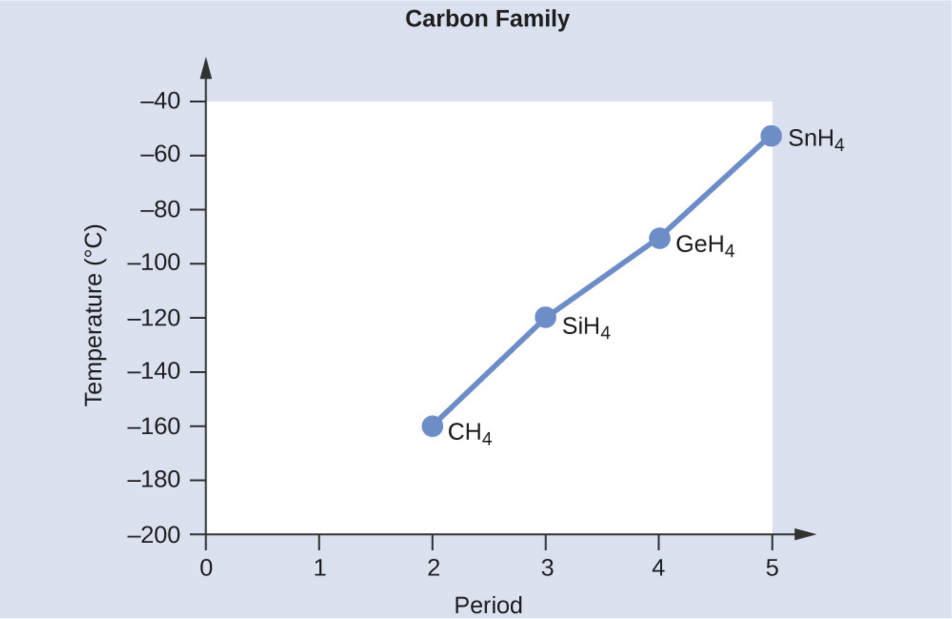

Figure 13.1f Boiling points of hydrogen compounds containing Group 14 elements (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct.

Exercise 13.1b

Check Your Learning Exercise (Text Version)
Order the following hydrocarbons from lowest to highest boiling point: C_3H_6, C_3C_8 and C_4C_{10}.

a. $C_3H_6 < C_3C_8 < C_4C_{10}$
b. $C_3C_8 < C_3H_6 < C_4C_{10}$
c. $C_4C_{10} < C_3H_6 < C_3C_8$
d. $C_3C_8 < C_3H_6 < C_4C_{10}$

Check Your Answer[1]

Source: "Exercise 13.1b" is adapted from "Example 10.1-1" from General Chemistry 1 & 2, a derivative

of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 13.1g) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behaviour is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

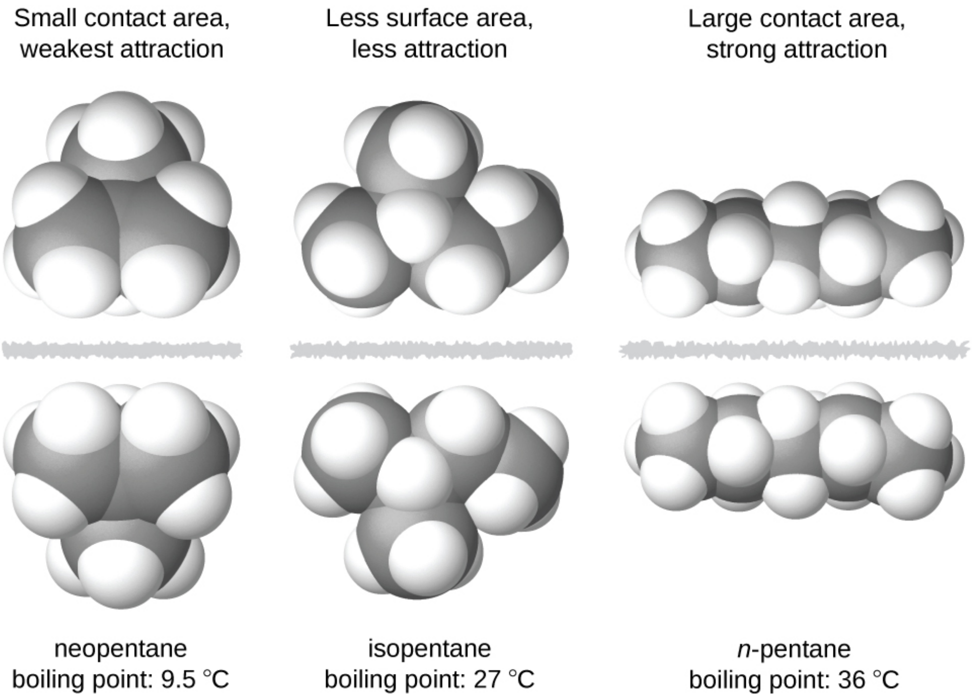

Figure 13.1g The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 13.1h, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally non-sticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

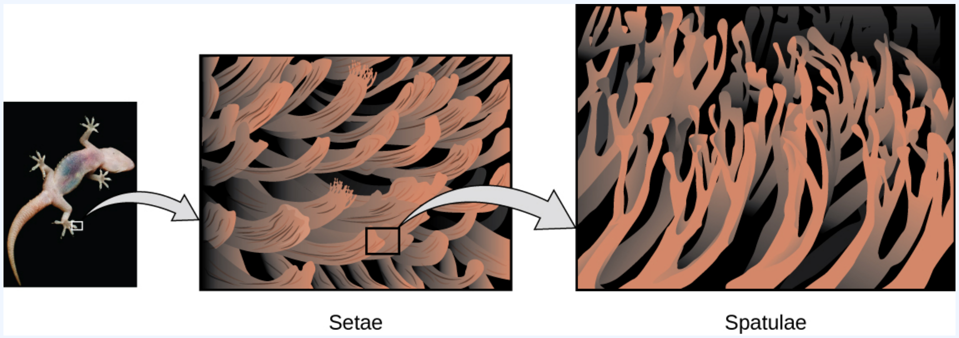

Figure 13.1h Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off" (credit photo: modification of work by JC+A, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).

Watch Smart materials (1 of 5): Gecko Adhesive fit for Spiderman (9 mins)

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a **dipole-dipole attraction**—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 13.1i.

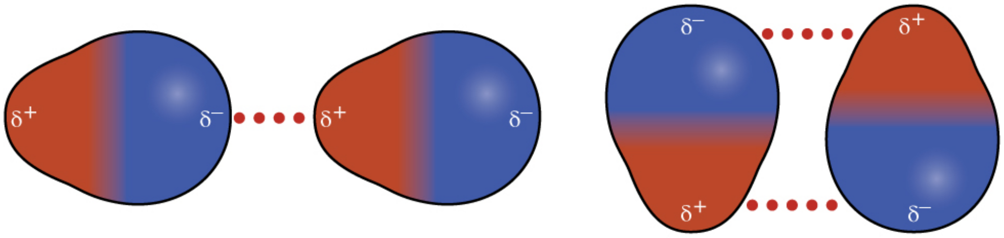

Figure 13.1i This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example 13.1b

Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Exercise 13.1c

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Check Your Answer[2]

Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include $HF\cdots HF$, $H_2O\cdots HOH$, and $H_3N\cdots HNH_2$, in which the hydrogen bonds are denoted by dots. Figure 13.1i illustrates hydrogen bonding between water molecules.

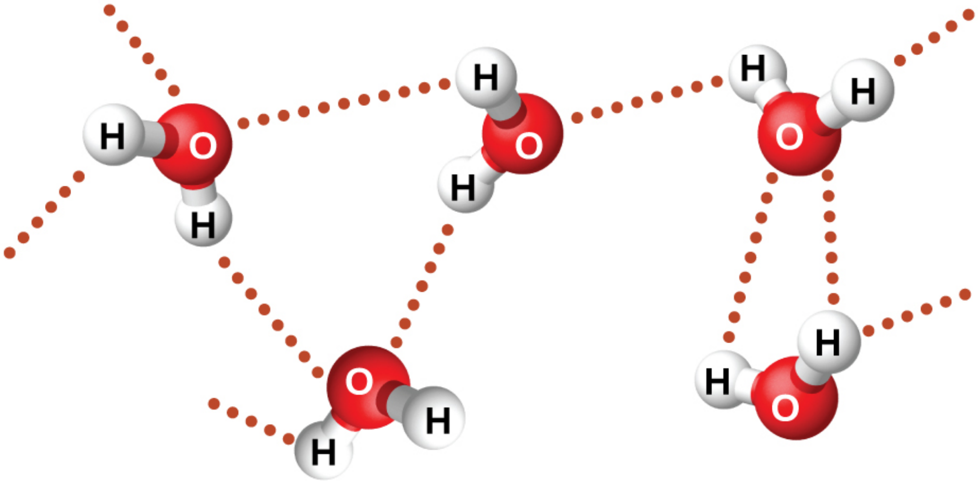

Figure 13.1j Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and

SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 13.1j. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.

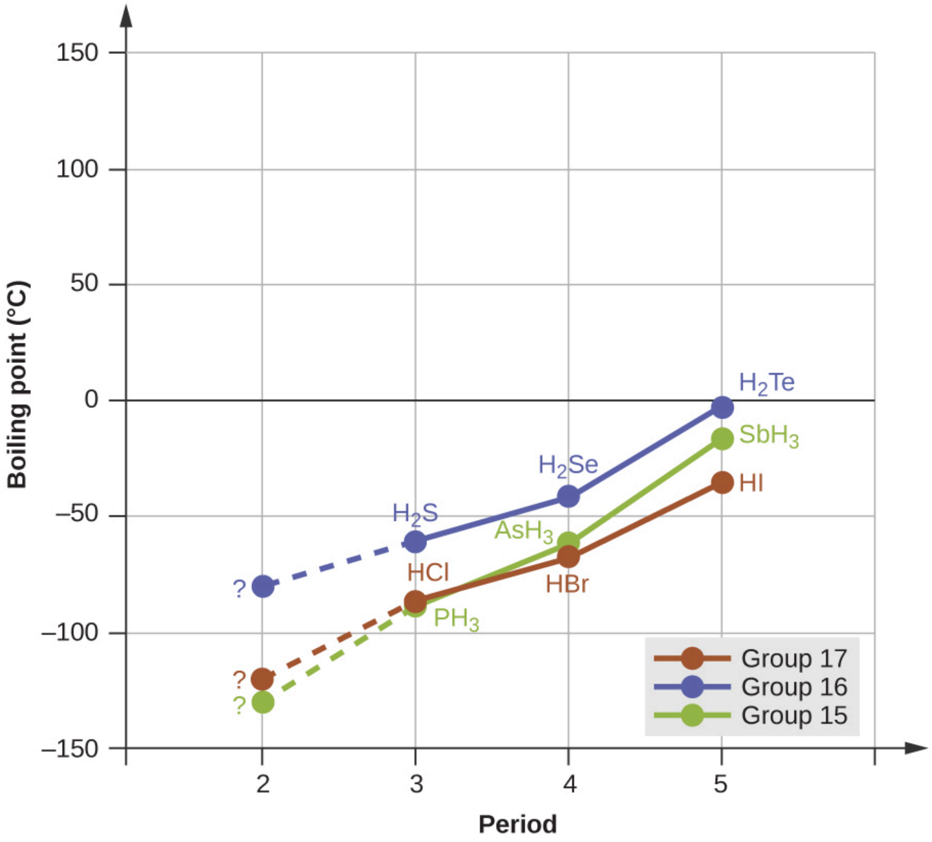

Figure 13.1k For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 13.1k. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

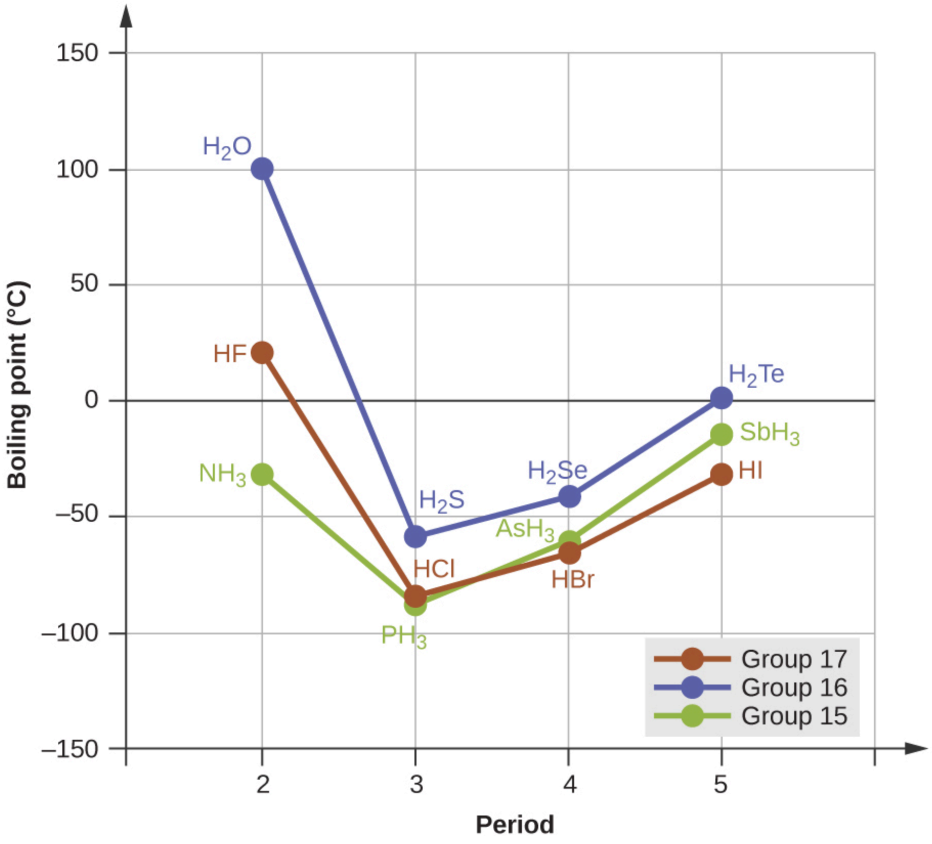

Figure 13.1l In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.1c

Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 13.1d

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Check Your Answer[3]

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 13.1l.

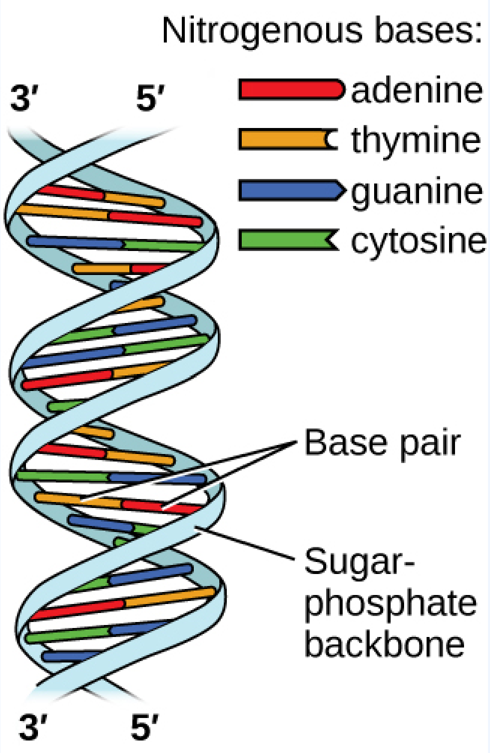

Figure 13.1m Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts, CC BY 4.0)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 13.1n.

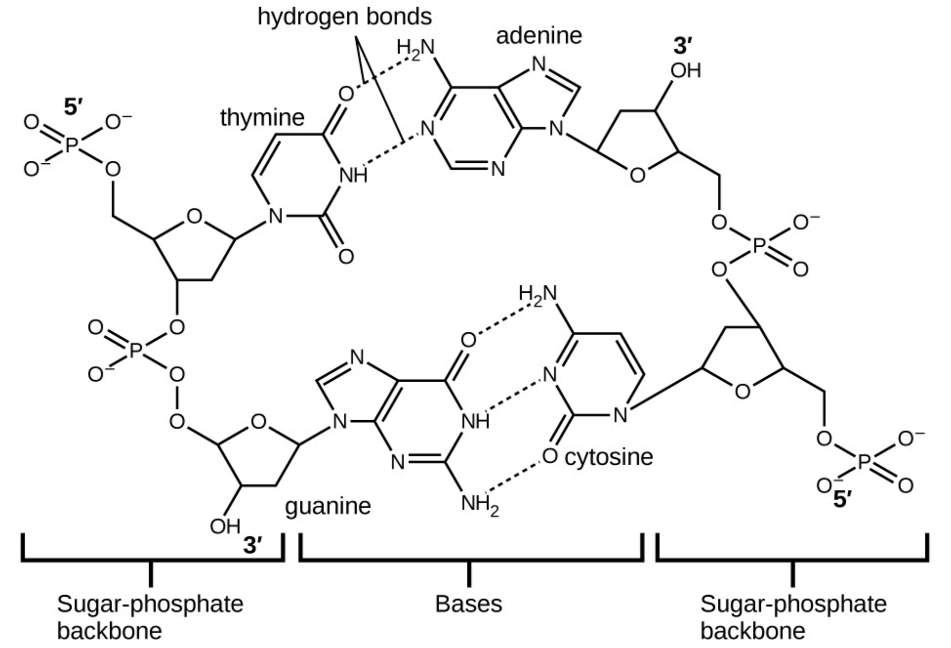

Figure 13.1n The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs." (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Attribution & References

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Notes

1. $C_3H_6 < C_3C_8 < C_4C_{10}$
2. ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

3. The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

13.2 PROPERTIES OF LIQUIDS

Learning Objectives

By the end of this section, you will be able to:

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The **viscosity** of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in Figure 13.2a, have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).

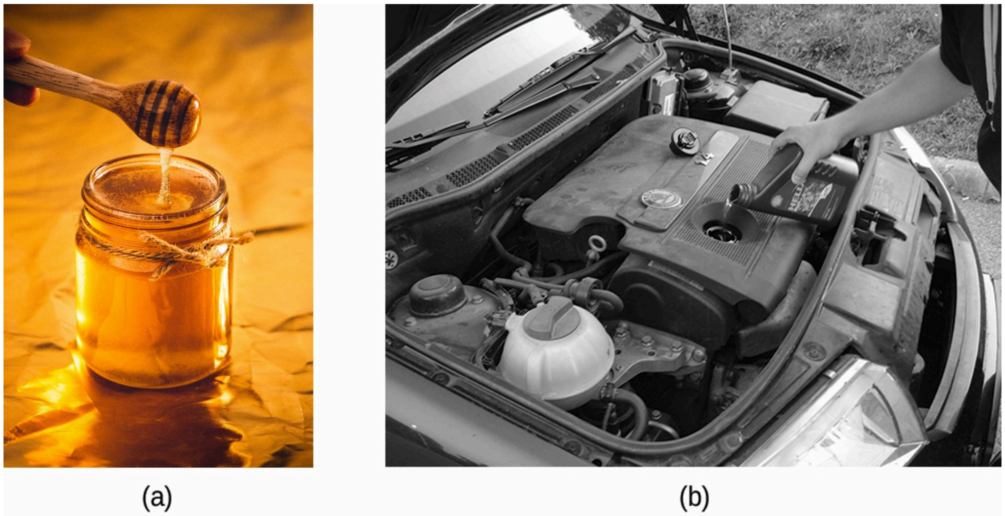

Figure 13.2a (a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: work by Art Rachen, Unsplash license; credit b: modification of work by David Nagy, CC BY 2.0)

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As Table 13.2a shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Table 13.2a Viscosities of Common Substances at 25 °C

Substance	Formula	Viscosity (mPa·s)
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of **cohesive forces**. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in Figure 13.2b, because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.

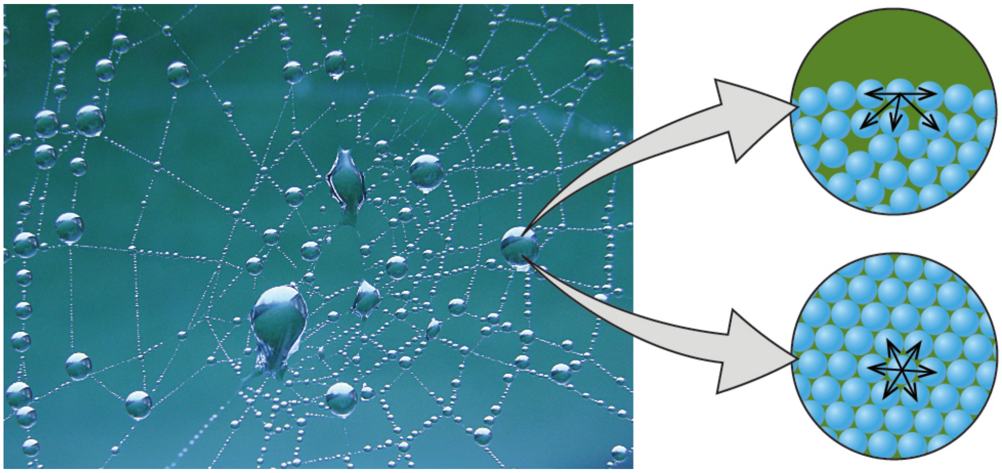

Figure 13.2b Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by OliBac, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in Table 13.2b. Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively “tough skin” that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in Figure 13.2c, even though they are denser than water, move on its surface because they are supported by the surface tension.

Table 13.2b Surface Tensions of Common Substances at 25 °C

Substance	Formula	Surface Tension (mN/m)
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99

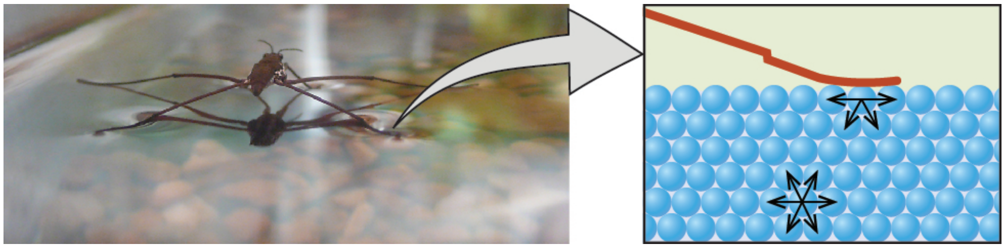

Figure 13.2c Surface tension (right) prevents this insect, a "water strider," from sinking into the water. (credit: modification of work by TimVickers, PD; in *Chemistry (OpenStax)*, CC BY 4.0).

The IMFs of attraction between two *different* molecules are called **adhesive forces**. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not "wet" the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop (Figure 13.2d).

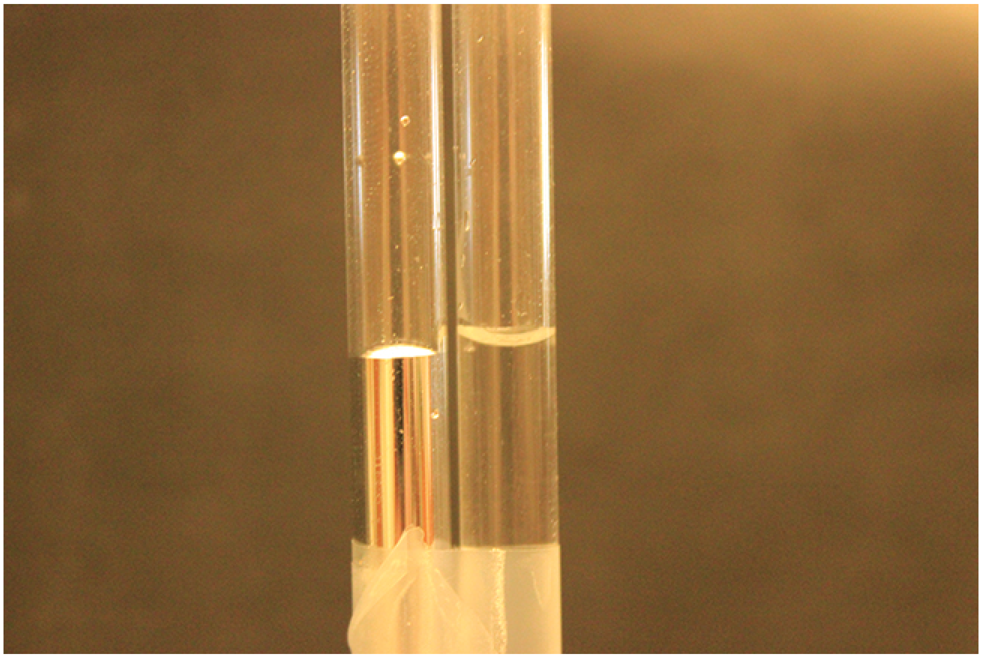

Figure 13.2d: Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

If you place one end of a paper towel in spilled wine, as shown in Figure 13.2e, the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of **capillary action**—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.

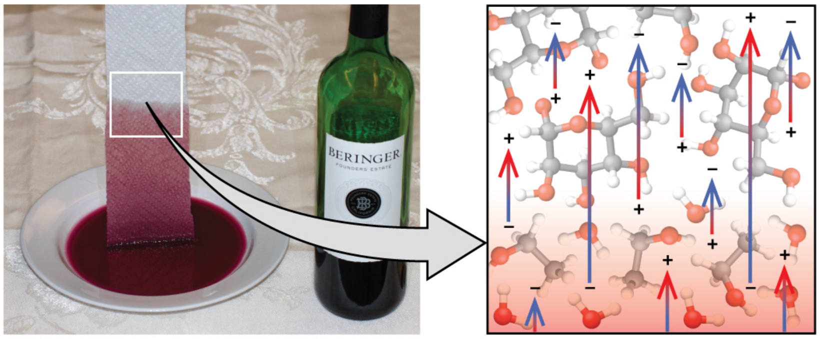

Figure 13.2e Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the –OH groups on the towel's cellulose fibres and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser in *Chemistry (OpenStax)*, CC BY 4.0).

Towels soak up liquids like water because the fibres of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many –OH groups. Water molecules are attracted to these –OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibres.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in Figure 13.2f. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.

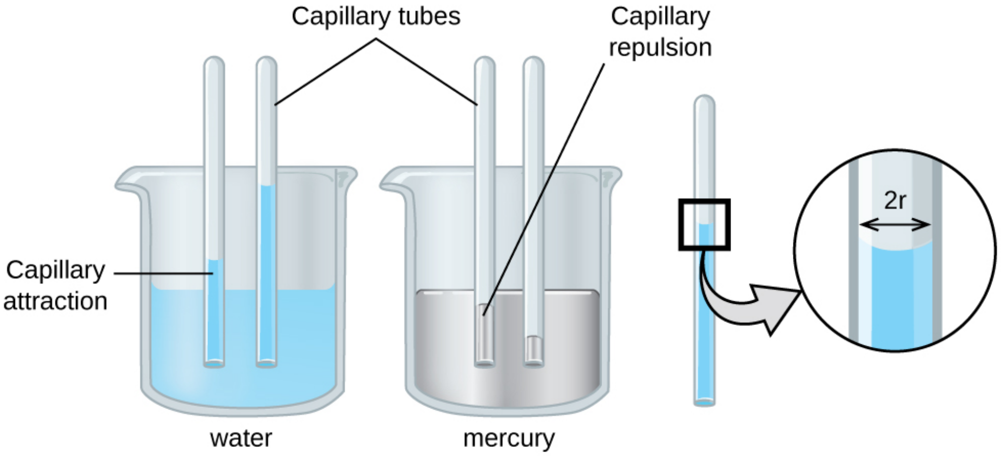

Figure 13.2f Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

$$h = \frac{2T\ \cos\theta}{r\rho g}$$

In this equation, h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube, T is the surface tension of the liquid, θ is the contact angle between the liquid and the tube, r is the radius of the tube, ρ is the density of the liquid, and g is the acceleration due to gravity, 9.8 m/s^2. When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0°. This is the situation for water rising in a glass tube.

Example 13.2a

Capillary Rise

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.25 mm?

For water, T = 71.99 mN/m and ρ = 1.0 g/cm^3.

Solution

The liquid will rise to a height *h* given by: $h = \dfrac{2T\ \cos\theta}{r\rho g}$

The Newton is defined as a kg m/s^2, and so the provided surface tension is equivalent to 0.07199 kg/s^2. The provided density must be converted into units that will cancel appropriately: ρ = 1000 kg/m^3. The diameter of the tube in meters is 0.00025 m, so the radius is 0.000125 m. For a glass tube immersed in water, the contact angle is θ = 0°, so cos θ = 1. Finally, acceleration due to gravity on the earth is g = 9.8 m/s^2. Substituting these values into the equation, and cancelling units, we have:

$$h = \frac{2(0.07199\ \mathrm{kg/s^2})}{(0.000125\ \mathrm{m})(1000\ \mathrm{kg/m^3})(9.8\ \mathrm{m/s^2})} = 0.12\ \mathrm{m} = 12\ \mathrm{cm}$$

Exercise 13.2a

Check Your Learning Exercise (Text Version)
Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?

a. 0.36 mm
b. 0.35 mm
c. 0.37 mm
d. 0.34 mm

Check Your Answer[1]

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Biomedical Applications of Capillary Action

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in the video below. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.

Watch Capillary Action Demonstration (1 min)

Key Equations

- $h = \dfrac{2T\ \cos\theta}{r\rho g}$

Attribution & References

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Notes

1. 0.36 mm

13.3 PHASE TRANSITIONS

Learning Objectives

By the end of this section, you will be able to:

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures, intermolecular attractive forces, and kinetic energy
- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

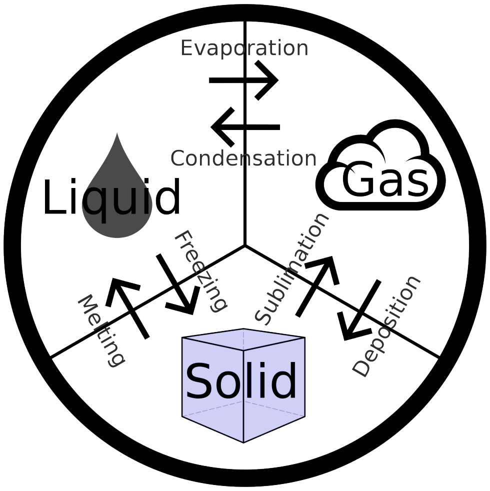


Figure 13.3a Phase Change Diagram: Condensation changes a gas to a liquid. Evaporation changes a liquid to a gas. Freezing changes a liquid to a solid. Melting changes a solid to a liquid. Sublimation changes a solid to a gas; whereas, deposition changes a gas to a solid. (credit: work by SiliconProphet, CC BY-SA 4.0).

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. Figure 13.3a shows a simple phase change diagram. The change from the gas phase to the liquid is called **condensation**. When the rate of condensation becomes equal to the rate of **vaporization**, neither the amount of the liquid nor the amount of the vapour in the container changes. The vapour in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a **dynamic equilibrium**, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapour in equilibrium with a liquid in a closed container at a given temperature is called the liquid's **vapour pressure** (or equilibrium vapour pressure). The area of the surface of the liquid in contact with a vapour and the size of the vessel have no effect on the vapour pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapour pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure 13.3b, and using a manometer to measure the increase in pressure that is due to the vapour in equilibrium with the condensed phase.

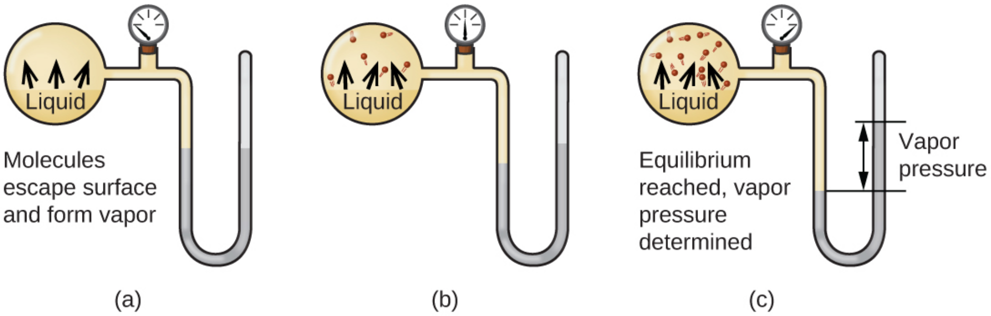


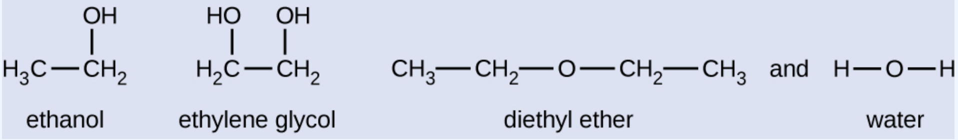
Figure 13.3b In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapour pressure of the gas is constant, although the vaporization and condensation processes continue (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapour pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favouring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapour pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapour pressures. The following example illustrates this dependence of vapour pressure on intermolecular attractive forces.

Example 13.3a

Explaining Vapour Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapour pressures in terms of types and extents of IMFs:



Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapour pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapour pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapour pressure than for either diethyl ether or ethanol. Ethylene glycol has two −OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapour pressure the lowest.

Exercise 13.3a

At 20 °C, the vapour pressures of several alcohols are given in this table. Explain these vapour pressures in terms of types and extents of IMFs for these alcohols:

Data Table for Exercise 13.3a

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapour Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Check Your Answer[1]

As temperature increases, the vapour pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure 13.3c. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapour pressure.

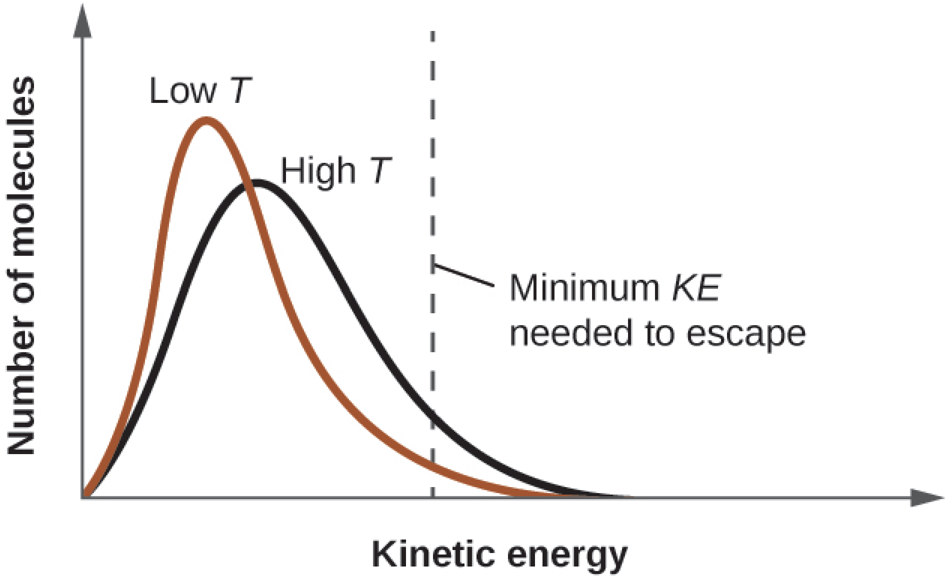


Figure 13.3c Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Boiling Points

When the vapour pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The **boiling point** of a liquid is the temperature at which its equilibrium vapour pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The **normal boiling point** of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure 13.3d shows the variation in vapour pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.

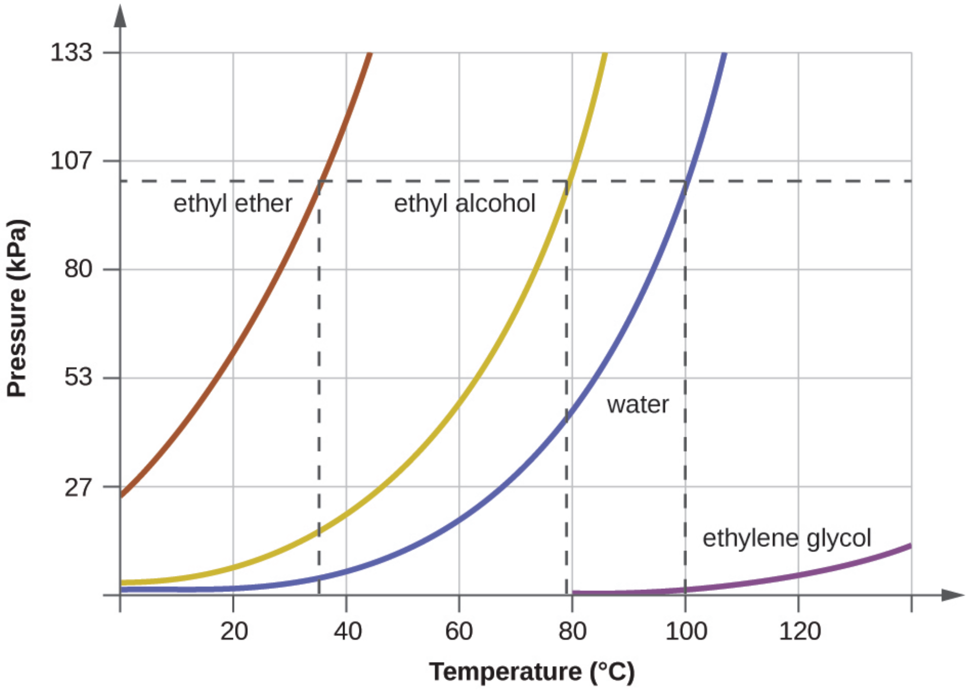


Figure 13.3d The boiling points of liquids are the temperatures at which their equilibrium vapour pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.3b

A Boiling Point at Reduced Pressure

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in Figure 13.3d to determine the boiling point of water at this elevation.

Solution

The graph of the vapour pressure of water versus temperature in Figure 13.3d indicates that the vapour pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapour pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

Exercise 13.3b

Check Your Learning Exercise (Text Version)
The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use Figure 13.3d to determine the approximate atmospheric pressure at the camp.

a. 40 kPa
b. 41 kPa
c. 39 kPa
d. 51kPa

Check Your Answer[2]

Source: "Exercise 13.3b" is adapted from "Example 10.3-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

The quantitative relation between a substance's vapour pressure and its temperature is described by the **Clausius-Clapeyron equation**:

$$P = Ae^{-\Delta H_{\text{vap}}/RT}$$

where ΔH_{vap} is the enthalpy of vaporization for the liquid, R is the gas constant, and $\ln A$ is a constant whose value depends on the chemical identity of the substance. This equation is often rearranged into logarithmic form to yield the linear equation:

$$\ln\,P = -\frac{\Delta H_{\text{vap}}}{RT}\ +\ \ln\,A$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the example exercises that follow. If at temperature T_1, the vapour pressure is P_1, and at temperature T_2, the vapour pressure is T_2, the corresponding linear equations are:

$$\ln\,P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1}\ +\ \ln\,A \qquad \text{and} \qquad \ln\,P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2}\ +\ \ln\,A$$

Since the constant, $\ln A$, is the same, these two equations may be rearranged to isolate $\ln A$ and then set them equal to one another:

$$\ln P_1 + \frac{\Delta H_{\text{vap}}}{RT_1} = \ln P_2 + \frac{\Delta H_{\text{vap}}}{RT_2}$$

which can be combined into:

$$\ln(\frac{P_2}{P_1}) = \frac{\Delta H_{\text{vap}}}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

Example 13.3c

Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapour pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapour pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

Solution

The enthalpy of vaporization, ΔH_{vap}, can be determined by using the Clausius-Clapeyron equation:

$$\ln\,(\frac{P_2}{P_1}) = \frac{\Delta H_{\text{vap}}}{R}\,(\frac{1}{T_1} - \frac{1}{T_2})$$

Since we have two vapour pressure-temperature values (T_1 = 34.0 °C = 307.2 K, P_1 = 10.0 kPa and T_2 = 98.8 °C = 372.0 K, P_2 = 100 kPa), we can substitute them into this equation and solve for ΔH_{vap}. Rearranging the Clausius-Clapeyron equation and solving for ΔH_{vap} yields:

$$\begin{aligned} \Delta H_{\text{vap}} &= \frac{R \times \ln\,(\frac{P_2}{P_1})}{(\frac{1}{T_1} - \frac{1}{T_2})} \\ &= \frac{(8.3145\ \text{J/mol·K}) \times \ln(\frac{100\ \text{kPa}}{10.0\ \text{kPa}})}{(\frac{1}{307.2\ \text{K}} - \frac{1}{372.0\ \text{K}})} \\ &= 33,800\ \text{J/mol} \\ &= 33.8\ \text{kJ/mol} \end{aligned}$$

Note that the pressure can be in any units, so long as they agree for both *P* values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

Exercise 13.3c

At 20.0 °C, the vapour pressure of ethanol is 5.95 kPa, and at 63.5 °C, its vapour pressure is 53.3 kPa. Use this information to estimate the enthalpy of vaporization for ethanol.

Check Your Answer[3]

Example 13.3d

Estimating Temperature (or Vapor Pressure)

For benzene (C_6H_6), the normal boiling point is 80.1 °C and the enthalpy of vaporization is 30.8 kJ/mol. What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa?

Solution

If the temperature and vapour pressure are known at one point, along with the enthalpy of vaporization, ΔH_{vap}, then the temperature that corresponds to a different vapour pressure (or the vapour pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right)=\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Since the normal boiling point is the temperature at which the vapour pressure equals atmospheric pressure at sea level, we know one vapour pressure-temperature value (T_1 = 80.1 °C = 353.3 K, P_1 = 101.3 kPa, ΔH_{vap} = 30.8 kJ/mol) and want to find the temperature (T_2) that corresponds to vapour pressure P_2 = 83.4 kPa. We can substitute these values into the Clausius-Clapeyron equation and then solve for T_2. Rearranging the Clausius-Clapeyron equation and solving for T_2 yields:

$$\begin{aligned} T_2 &= \left(\frac{-R \times \ln\left(\frac{P_2}{P_1}\right)}{\Delta H_{\text{vap}}} + \frac{1}{T_1}\right)^{-1} \\ &= \left(\frac{-(8.3145\ \text{J/mol·K}) \times \ln\left(\frac{83.4\ \text{kPa}}{101.3\ \text{kPa}}\right)}{30{,}800\ \text{J/mol}} + \frac{1}{353.3\ \text{K}}\right)^{-1} \\ &= 346.9\ \text{K or } 73.8\ ^\circ\text{C} \end{aligned}$$

Exercise 13.3d

For acetone $(CH_3)_2CO$, the normal boiling point is 56.5 °C and the enthalpy of vaporization is 31.3 kJ/mol. What is the vapour pressure of acetone at 25.0 °C?

Check Your Answer[4]

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. For example, the vaporization of water at standard temperature is represented by:

$$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g) \qquad \Delta H_{\text{vap}} = 44.01\ \text{kJ/mol}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l) \qquad \Delta H_{\text{con}} = -\Delta H_{\text{vap}} = -44.01\ \text{kJ/mol}$$

Example 13.3e

Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure 13.3e). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at T = 37 °C (normal body temperature); ΔH_{vap} = 43.46 kJ/mol at 37 °C.

Figure 13.3e Evaporation of sweat helps cool the body. (credit: work by Kullez, CC BY 2.0)

Solution

We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

$$1.5\ \cancel{\text{L}} \times \frac{1000\ \cancel{\text{g}}}{1\ \cancel{\text{L}}} \times \frac{1\ \cancel{\text{mol}}}{18\ \cancel{\text{g}}} \times \frac{43.46\ \text{kJ}}{1\ \cancel{\text{mol}}} = 3.6 \times 10^{3}\ \text{kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

Exercise 13.3e

How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3, at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Check Your Answer[5]

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state or **melting**. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 13.3f).

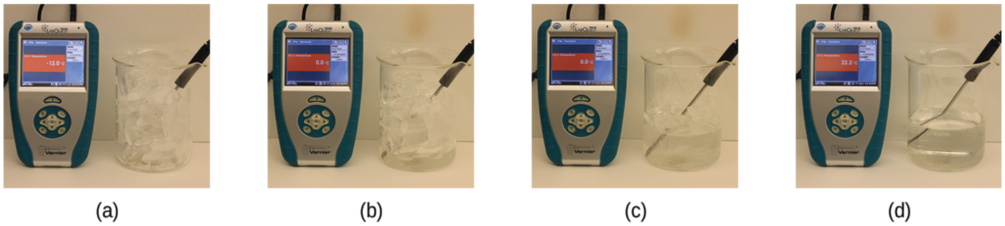


Figure 13.3f (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of melting and **freezing** occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the **melting point** of the solid or the **freezing point** of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l) \qquad \Delta H_{\text{fus}} = 6.01\ \text{kJ/mol}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(s) \qquad \Delta H_{\text{frz}} = -\Delta H_{\text{fus}} = -6.01\ \text{kJ/mol}$$

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapour forms (Figure 13.3g). The reverse of sublimation is called **deposition**, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.

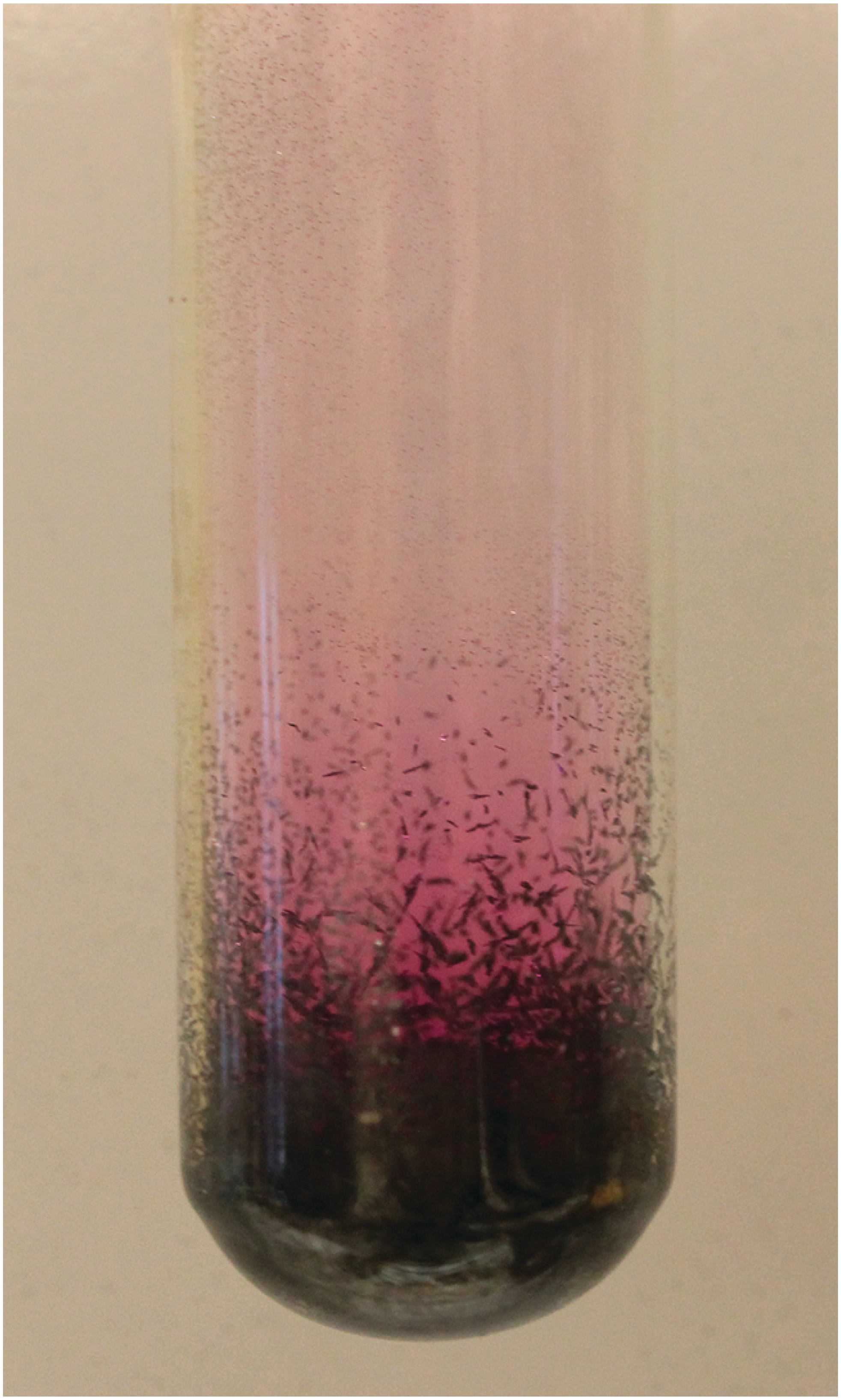


Figure 13.3g Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub}, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H_{\text{sub}} = 26.1\ \text{kJ/mol}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO_2}(s) \qquad \Delta H_{\text{dep}} = -\Delta H_{\text{sub}} = -26.1\ \text{kJ/mol}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modelled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law. Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 13.3h. For example:

$$\begin{array}{rlr} \text{solid} & \longrightarrow \text{liquid} & \Delta H_{\text{fus}} \\ \text{liquid} & \longrightarrow \text{gas} & \Delta H_{\text{vap}} \\ \hline \text{solid} & \longrightarrow \text{gas} & \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \end{array}$$

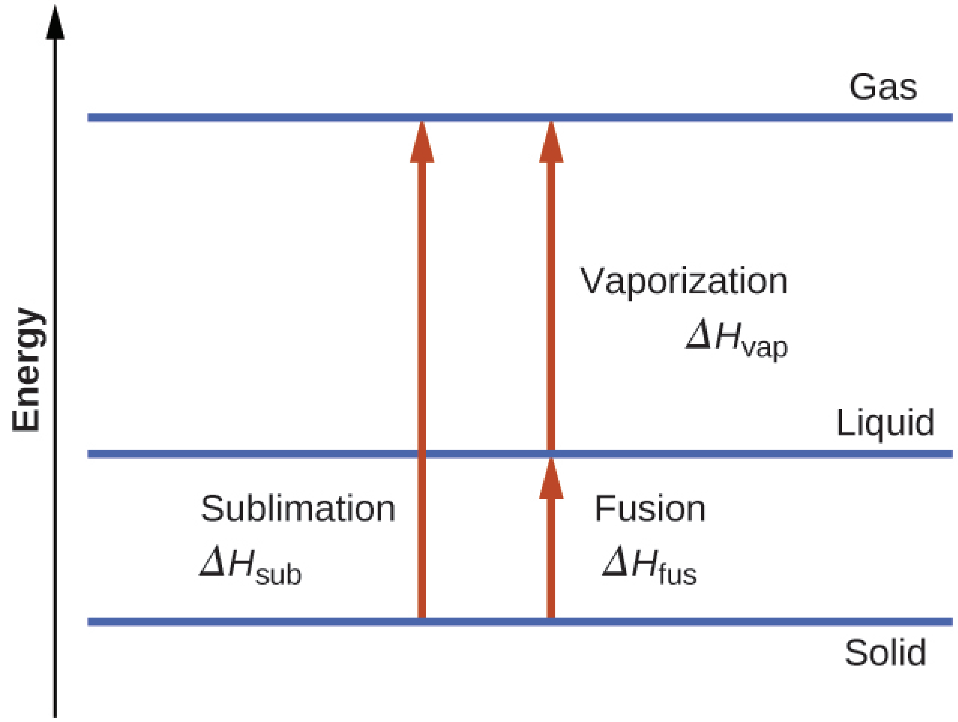


Figure 13.3h For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Heating and Cooling Curves

In the chapter on thermochemistry, the relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, was introduced:

$$q = mc\Delta T$$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance is heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. Figure 13.3i shows a typical heating curve.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behaviour is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.

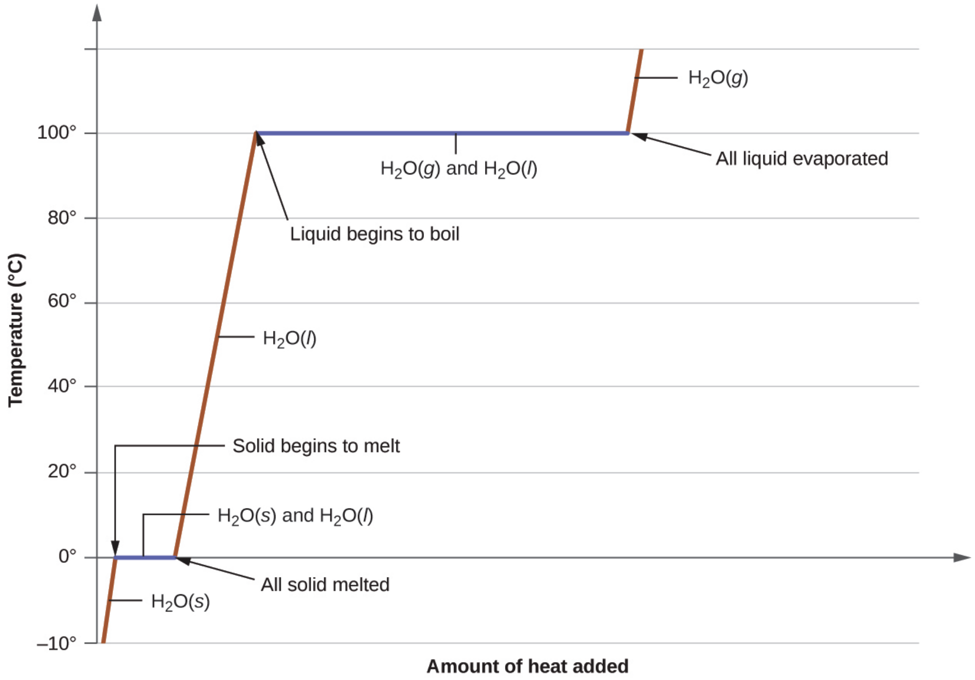


Figure 13.3i A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.3f

Total Heat Needed to Change Temperature and Phase for a Substance

How much heat is required to convert 135 g of ice at −15 °C into water vapour at 120 °C?

Solution

The transition described involves the following steps:

1. Heat ice from −15 °C to 0 °C
2. Melt ice
3. Heat water from 0 °C to 100 °C
4. Boil water
5. Heat steam from 100 °C to 120 °C

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = m \times c \times \Delta T$ (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by $q = n \times \Delta H$.

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

$$\begin{aligned} q_{\text{total}} = \; & (m{\cdot}c{\cdot}\Delta T)_{\text{ice}} + n{\cdot}\Delta H_{\text{fus}} + (m{\cdot}c{\cdot}\Delta T)_{\text{water}} + n{\cdot}\Delta H_{\text{vap}} + (m{\cdot}c{\cdot}\Delta T)_{\text{steam}} \\ = \; & (135\ \text{g} \times 2.09\ \text{J/g}{\cdot}\,^\circ\text{C} \times 15\,^\circ\text{C}) \\ & + (135\ \text{g} \times \frac{1\ \text{mol}}{18.02\ \text{g}} \times 6.01\ \text{kJ/mol}) \\ & + (135\ \text{g} \times 4.18\ \text{J/g}{\cdot}\,^\circ\text{C} \times 100\,^\circ\text{C}) \\ & + (135\ \text{g} \times \frac{1\ \text{mol}}{18.02\ \text{g}} \times 40.67\ \text{kJ/mol}) \\ & + (135\ \text{g} \times 1.84\ \text{J/g}{\cdot}\,^\circ\text{C} \times 20\,^\circ\text{C}) \\ = \; & 4230\ \text{J} + 45.0\ \text{kJ} + 56,500\ \text{J} + 305\ \text{kJ} + 4970\ \text{J} \end{aligned}$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

$$= 4.23\ \text{kJ} + 45.0\ \text{kJ} + 56.5\ \text{kJ} + 305\ \text{kJ} + 4.97\ \text{kJ} = 416\ \text{kJ}$$

Exercise 13.3f

What is the total amount of heat released when 94.0 g water at 80.0 °C cools to form ice at −30.0 °C?

Check Your Answer[6]

Exercise 13.3g

Practice using the following PhET simulation: Energy Forms and Changes

Key Equations

- $P = Ae^{-\Delta H_{\text{vap}}/RT}$
- $\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A$
- $\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Attribution & References

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Notes

1. All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapour pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapour pressures decrease as observed: $P_{\text{methanol}} > P_{\text{ethanol}} > P_{\text{propanol}} > P_{\text{butanol}}$.
2. 40 kPa
3. 47,782 J/mol = 47.8 kJ/mol
4. 30.1 kPa
5. 28 kJ
6. 40.5 kJ

13.4 PHASE DIAGRAMS

Learning Objectives

By the end of this section, you will be able to:

- Explain the construction and use of a typical phase diagram
- Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions resulting from changes in these properties
- Describe the supercritical fluid phase of matter

In the previous module, the variation of a liquid's equilibrium vapour pressure with temperature was described. Considering the definition of boiling point, plots of vapour pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A **phase diagram** combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in Figure 13.4a.

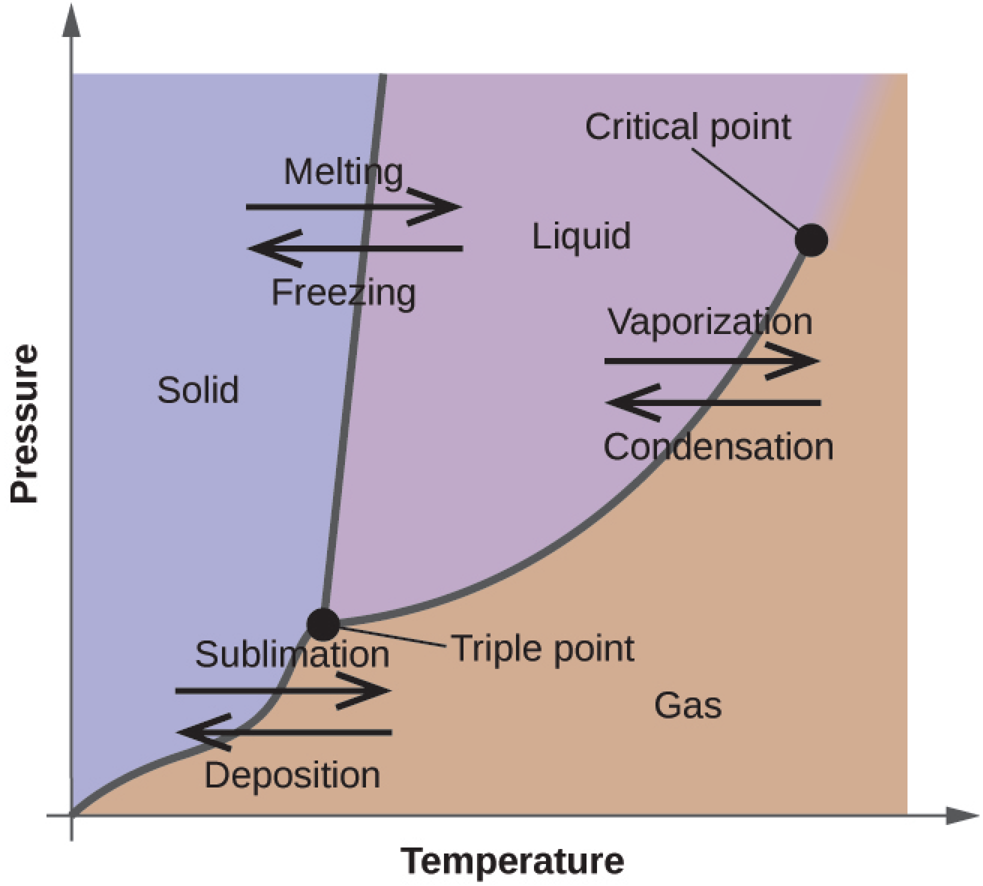

Figure 13.4a The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram (credit: *Chemistry (OpenStax)*, CC BY 4.0).

To illustrate the utility of these plots, consider the phase diagram for water shown in Figure 13.4b.

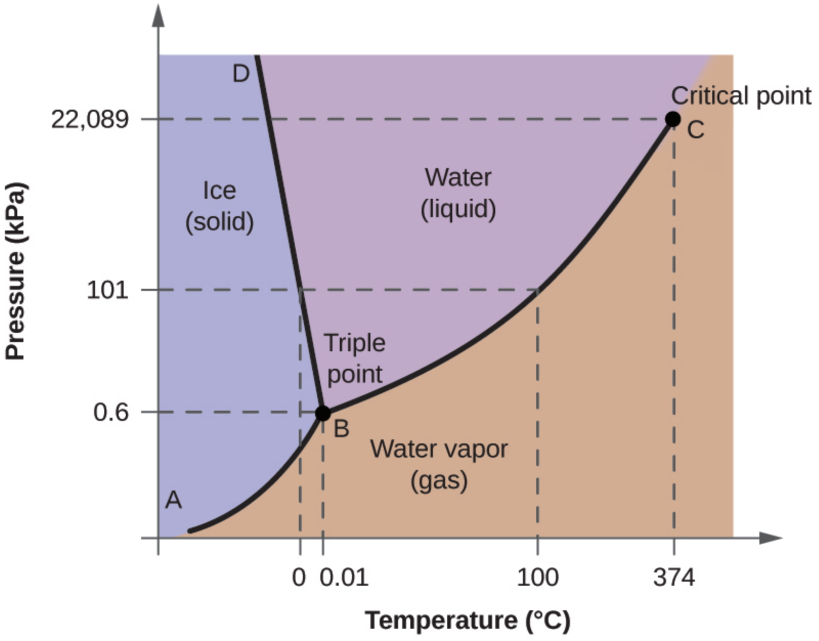

Figure 13.4b The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties (credit: *Chemistry (OpenStax)*, CC BY 4.0).

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of −10 °C correspond to the region of the diagram labeled "ice." Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50 °C correspond to the "water" region—here, water exists only as a liquid. At 25 kPa and 200 °C, water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in Figure 13.4b is the plot of vapour pressure versus temperature as described in the previous module of this chapter. This "liquid-vapour" curve separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapour curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapour curve, labeled AB in Figure 13.4b, indicates the temperatures and pressures at which ice and water vapour are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in Figure 13.4b, we would see that ice has a vapour pressure of about 0.20 kPa at −10 °C. Thus, if we place a frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the “freeze-drying” process often used to preserve foods, such as the ice cream shown in Figure 13.4c.

Figure 13.4c Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: work by Iwao, CC BY 2.0)

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behaviour is partly responsible for the movement of glaciers, like the one shown in Figure 13.4d. The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.

Figure 13.4d The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: work by NASA, Image use policy)

The point of intersection of all three curves is labeled B in Figure 13.4b. At the pressure and temperature represented by this point, all three phases of water coexist in equilibrium. This temperature-pressure data pair is called the **triple point**. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.

Example 13.4a

Determining the State of Water

Using the phase diagram for water given in Figure 13.4b, determine the state of water at the following temperatures and pressures:

a. −10 °C and 50 kPa
b. 25 °C and 90 kPa
c. 50 °C and 40 kPa
d. 80 °C and 5 kPa
e. −10 °C and 0.3 kPa
f. 50 °C and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure gave are as follows:

a. solid;
b. liquid;
c. liquid;
d. gas;
e. solid;
f. gas.

Exercise 13.4a

What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? Is the pressure held at 50 kPa?

Check Your Answer[1]

Consider the phase diagram for carbon dioxide shown in Figure 13.4e as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimes to yield gaseous CO_2. Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.

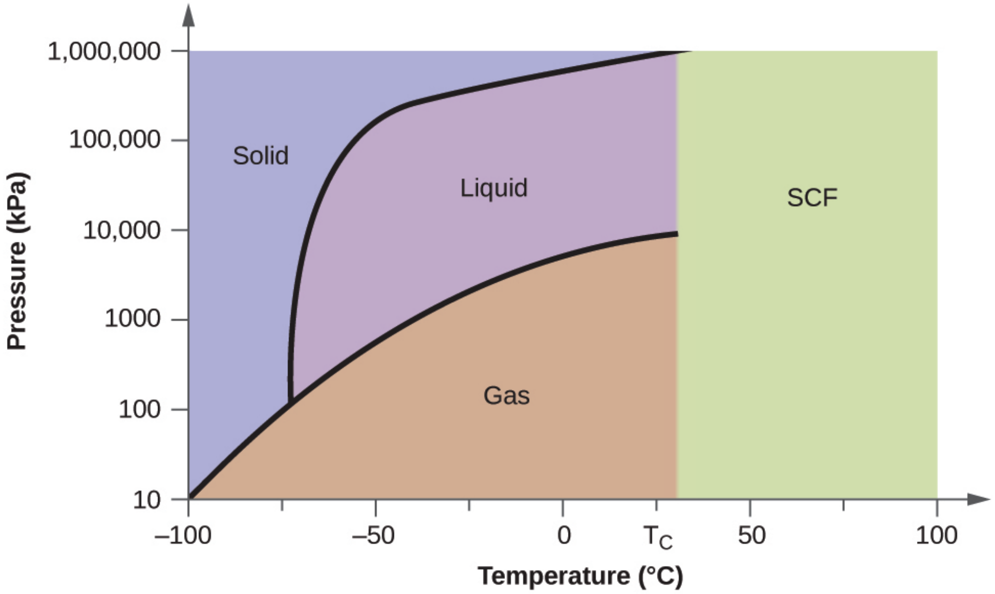

Figure 13.4e The pressure and temperature axes on this phase diagram of carbon dioxide are not drawn to constant scale in order to illustrate several important properties (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 13.4b

Determining the State of Carbon Dioxide

Using the phase diagram for carbon dioxide shown in Figure 13.4e, determine the state of CO_2 at the following temperatures and pressures:

a. −30 °C and 2000 kPa
b. −60 °C and 1000 kPa
c. −60 °C and 100 kPa
d. 20 °C and 1500 kPa
e. 0 °C and 100 kPa
f. 20 °C and 100 kPa

Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO_2 at each temperature and pressure given are as follows:

a. liquid;
b. solid;
c. gas;
d. liquid;
e. gas;
f. gas.

Exercise 13.4b

Determine the phase changes carbon dioxide undergoes when its temperature is varied, thus holding its pressure constant at 1500 kPa? At 500 kPa? At what approximate temperatures do these phase changes occur?

Check Your Answer[2]

Supercritical Fluids

If we place a sample of water in a sealed container at 25 °C, remove the air, and let the vaporization-condensation equilibrium establish itself, we are left with a mixture of liquid water and water vapour at a pressure of 0.03 atm. A distinct boundary between the more dense liquid and the less dense gas is clearly observed. As we increase the temperature, the pressure of the water vapour increases, as described by the liquid-gas curve in the phase diagram for water (Figure 13.4b), and a two-phase equilibrium of liquid and gaseous phases remains. At a temperature of 374 °C, the vapour pressure has risen to 218 atm, and any further increase in temperature results in the disappearance of the boundary between liquid and vapour phases. All of the water in the container is now present in a single phase whose physical properties are intermediate between those of the gaseous and liquid states. This phase of matter is called a **supercritical fluid**, and the temperature and pressure above which this phase exists is the **critical point** (see video below). Above its critical temperature, a gas cannot be liquefied no matter how much pressure is applied. The pressure required to liquefy a gas at its critical temperature is called critical pressure. The critical temperatures and critical pressures of some common substances are given in Table 13.4a.

Table 13.4a Critical temperatures and pressures of common substances.

Substance	Critical Temperature (K)	Critical Pressure (atm)
hydrogen	33.2	12.8
nitrogen	126.0	33.5
oxygen	154.3	49.7
carbon dioxide	304.2	73.0
ammonia	405.5	111.5
sulfur dioxide	430.3	77.7
water	647.1	217.7

Watch Supercritical CO2 (5 mins)

Like a gas, a supercritical fluid will expand and fill a container, but its density is much greater than typical gas densities, typically being close to those for liquids. Similar to liquids, these fluids are capable of dissolving nonvolatile solutes. They exhibit essentially no surface tension and very low viscosities, however, so they can more effectively penetrate very small openings in a solid mixture and remove soluble components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, being used to decaffeinate coffee, remove fats from potato chips, and extract flavour and fragrance compounds from citrus oils. It is nontoxic, relatively inexpensive, and not considered to be a pollutant. After use, the CO_2 can be easily recovered by reducing the pressure and collecting the resulting gas.

Example 13.4c

The Critical Temperature of Carbon Dioxide

If we shake a carbon dioxide fire extinguisher on a cool day (18 °C), we can hear liquid CO_2 sloshing around inside the cylinder. However, the same cylinder appears to contain no liquid on a hot summer day (35 °C). Explain these observations.

Solution

On a cool day, the temperature of the CO_2 is below the critical temperature of CO_2, 304 K or 31 °C (Table 13.4a), so liquid CO_2 is present in the cylinder. On a hot day, the temperature of the CO_2 is greater than its critical temperature of 31 °C. Above this temperature, no amount of pressure can liquefy CO_2 so no liquid CO_2 exists in the fire extinguisher.

Exercise 13.4c

Check Your Learning Exercise (Text Version)
Ammonia can be liquefied by compression at room temperature; oxygen cannot be liquefied under these conditions. Why do the two gases exhibit different behaviour?

a. The critical temperature of ammonia is 405.5 K, which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.
b. The critical temperature of ammonia is 405.5 K, which is lower than room temperature. The critical temperature of oxygen is above room temperature; thus oxygen cannot be liquefied at room temperature.
c. Ammonia is at the lower level in the periodic table compared to Oxygen; thus oxygen cannot be liquefied at room temperature.
d. Oxygen is present in abundant compared to oxygen; thus oxygen cannot be liquefied at room temperature.

Check Your Answer[3]

Source: "Exercise 13.4c" is adapted from "Example 10.4-3" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Decaffeinating Coffee Using Supercritical CO_2

Coffee is the world's second most widely traded commodity, following only petroleum. Across the globe, people love coffee's aroma and taste. Many of us also depend on one component of coffee—caffeine—to help us get going in the morning or stay alert in the afternoon. But late in the day, coffee's stimulant effect can keep you from sleeping, so you may choose to drink decaffeinated coffee in the evening.

Since the early 1900s, many methods have been used to decaffeinate coffee. All have advantages and disadvantages, and all depend on the physical and chemical properties of caffeine. Because caffeine is a somewhat polar molecule, it dissolves well in water, a polar liquid. However, since many of the other 400-plus compounds that contribute to coffee's taste and aroma also dissolve in H_2O, hot water decaffeination processes can also remove some of these compounds, adversely affecting the smell and taste of the decaffeinated coffee. Dichloromethane (CH_2Cl_2) and ethyl acetate ($CH_3CO_2C_2H_5$) have similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavour and aroma components, and their use requires long extraction and cleanup times. Because both of these solvents are toxic, health concerns have been raised regarding the effect of residual solvent remaining in the decaffeinated coffee.

Supercritical fluid extraction using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method (Figure 13.4f). At temperatures above 304.2 K and pressures above 7376 kPa, CO_2 is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97−99% of the caffeine, leaving coffee's flavour and aroma compounds intact. Because CO_2 is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract. The caffeine recovered from coffee beans via this process is a valuable product that can be used subsequently as an additive to other foods or drugs.

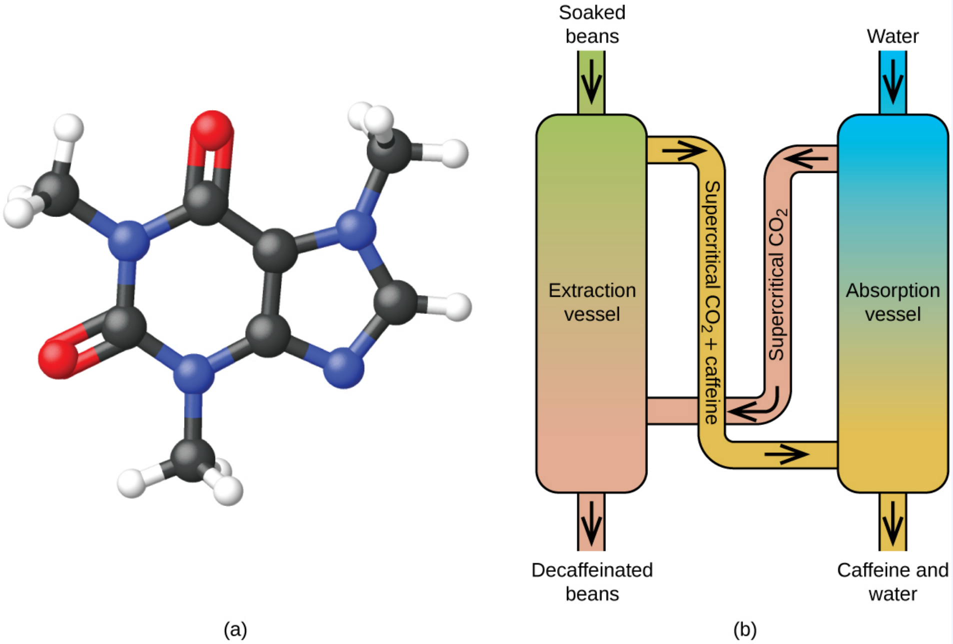

Figure 13.4f (a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities. (b) The schematic shows a typical decaffeination process involving supercritical car (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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Notes

1. At 0.3 kPa: $\text{s} \longrightarrow \text{g}$ at −58 °C. At 50 kPa: $\text{s} \longrightarrow \text{l}$ at 0 °C, $\text{l} \longrightarrow \text{g}$ at 78 °C
2. at 1500 kPa: $\text{s} \longrightarrow \text{l}$ at −45 °C, $\text{l} \longrightarrow \text{g}$ at −10 °C;
   at 500 kPa: $\text{s} \longrightarrow \text{g}$ at −58 °C
3. The critical temperature of ammonia is 405.5 K, which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.

13.5 WATER: A SPECIAL LIQUID

Learning Objective

By the end of this section, you will be able to:

- To describe the unique characteristics of water in terms of its structure

Water: A Special Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in **solution**. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small **molecule**. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favourable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighbouring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of arrangement in the ice crystal. This arrangement requires that the molecules are somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

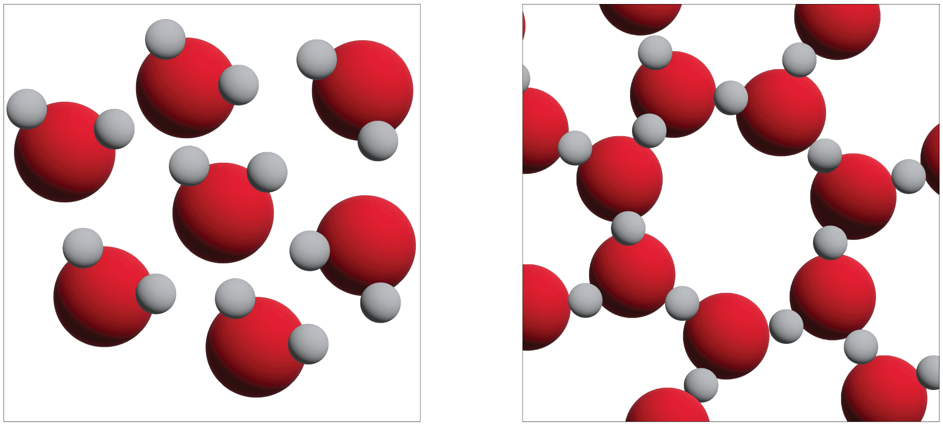


Figure 13.5a Three-dimensional views of a typical local structure of liquid water (left) and ice (right). (credit: graphics by Revathi Mahadevan, CC BY 4.0)

In figure 13.5a we can see three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of **hydrogen bonding** in a uniform, extended crystal lattice. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion. Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by "antifreeze" and why unprotected pipes in houses break if they are allowed to freeze.

Watch Why does ice float in water? (3:55 min)

Watch The Properties of Water (4:58 min)

Structure of the Water Molecule

Because oxygen is such an electronegative element, the two covalent OH bonds in water are polar and are formed by the overlap of the 1*s* orbital of hydrogen with an unpaired 2*p* orbital of oxygen.**Valence shell electron-pair repulsion theory (VSEPR theory)** (see chapter 11.7) tells us that the water molecule has a bent shape with bond angles of approximately 105^0, making water a very **polar molecule**. These bond angles and bent shape result in a partial negative charge on the oxygen atom and a partial positive charge on each hydrogen atom (figure 13.5b) (Hein et al., 2013, p. 298).

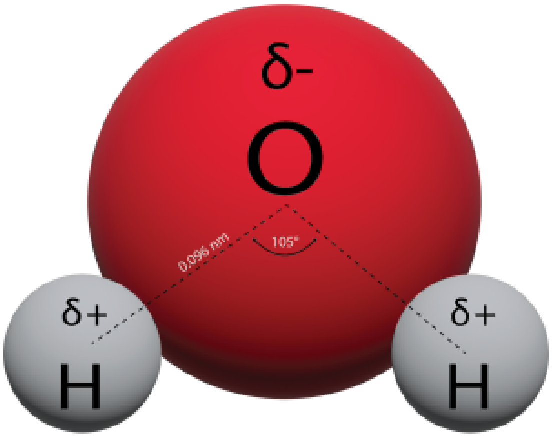


Figure 13.5b The figure illustrates the water molecular structure, O-H bond length, and bond angle. (credit: graphics by Revathi Mahadevan, CC BY 4.0)

Water's influence on the world around us is affected by these properties. Isn't it fascinating that such a small molecule can have such a big impact?

Scientists in Action: Dr. Katsuko Saruhashi

Japanese geochemist Katsuko Saruhashi (March 1920 – September 2007) was the first woman to earn a doctorate degree in chemistry from the prestigious University of Tokyo. Interested in environmental toxicology from an early age, Katsuko conducted research and created tools that let her take the first measurements of carbon dioxide (CO_2) levels in seawater. This groundbreaking research allowed her and her team to demonstrate that previous hypotheses based on the idea that elevated CO_2 levels found in seawater could not be blamed on the dissolution of calcium carbonate, and instead were related to global warming caused by human activity. Among her many honours, she was the first woman elected to the Science Council of Japan and the first woman to be awarded the Miyake prize for geochemistry.

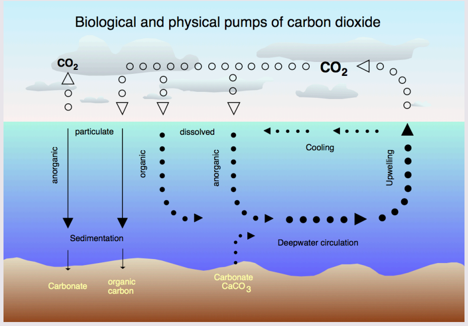


Figure 13.5c Working of the biological and physical pumps of carbon dioxide. (credit: work by Hannes Grobe, CC BY-SA 2.5)

Read more about Katsuko Saruhashi in the article “Meet Katsuko Saruhashi, a resilient geochemist who detected nuclear fallout in the Pacific” [New Tab]

Indigenous Perspective: Sea Ice and Snow

Figure 13.5d Sea ice in the Arctic (credit: work by Matti&Keti, CC BY-SA 4.0)

Inuit survival has always depended upon the important and stable coverage of the Arctic Ocean in ice. Sea ice (figure 13.5d) is an essential gateway to freedom for the Inuit, and it makes life possible due to its many unique chemical properties. On the other hand, the chemistry of snow is equally important, especially given the fact that it covers the Arctic for most of the year. The chemical properties of snow make it an important insulator, building material, and an important cultural symbol for the Inuit.

To learn more about the chemistry of both sea ice and snow, read the following articles:

- Sea Ice: Essential for northern survival [New Tab]
- Snow: Making life possible in the Arctic [New Tab]

Watch **The science of snowflakes (4:29 min)**

Attribution & References

Except where otherwise noted, this section is adapted by Gregory A. Anderson from “8.2: Solids and Liquids” In *Basics of General, Organic and Biological Chemistry (LibreTexts)* by David W. Ball, John W. Hill, and Rhonda J. Scott, licensed under CC BY-NC-SA 3.0

Reference

Hein, M., Pattison, S., Arena, S., & Best, L. (2013). Introduction to general, organic, and biochemistry(11th ed.). John Wiley & Sons, Inc.

CHAPTER 13 - SUMMARY

13.1 – Intermolecular Forces

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behaviour of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

13.2 – Properties of Liquids

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid's viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

13.3 – Phase Transitions

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

13.4 – Phase Diagrams

The temperature and pressure conditions at which a substance exists in solid, liquid, and gaseous states are summarized in a phase diagram for that substance. Phase diagrams are combined plots of three pressure-temperature equilibrium curves: solid-liquid, liquid-gas, and solid-gas. These curves represent the relationships between phase-transition temperatures and pressures. The point of intersection of all three curves represents the substance's triple point—the temperature and pressure at which all three phases are in equilibrium. At pressures below the triple point, a substance cannot exist in the liquid state, regardless of its temperature. The terminus of the liquid-gas curve represents the substance's critical point, the pressure and temperature above which a liquid phase cannot exist.

13.5 – Water: A Special Liquid

Water has many unique properties that not only allow life on Earth to flourish, but make it the most common solvent used in chemistry labs. The polar nature of the water (H_2O) molecule, as determined by VSEPR theory, impart these properties to water; for instance, solid H_2O (ice) is less dense than liquid H_2O, a rare property for a liquid to possess. As well, although it is a small molecule, water requires a relatively large amount of energy in order to change physical states.

Attribution & References

Except where otherwise noted, this page is adapted by Gregory A. Anderson from:

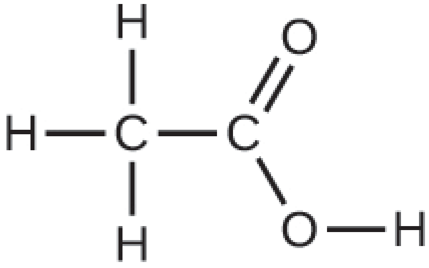
- "10.1 Intermolecular Forces", "10.2 Properties of Liquids", "10.3 Phase Transitions", "10.4 Phase Diagrams", In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* . / Extracted and reused the key-takeaways/summary from each section used.
- "8.2: Solids and Liquids" In *Basics of General, Organic and Biological Chemistry (LibreTexts)* by David W. Ball, John W. Hill, and Rhonda J. Scott, licensed under CC BY-NC-SA 3.0

CHAPTER 13 - REVIEW

13.1 – Intermolecular Forces

1. In terms of their bulk properties, how do liquids and solids differ? How are they similar? **Check Answer:** [1]
2. In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?
3. In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases? **Check Answer:** [2]
4. Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.
5. What is the evidence that all neutral atoms and molecules exert attractive forces on each other? **Check Answer:** [3]
6. Open the PhET States of Matter Simulation to answer the following questions:
   a. Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
   b. For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
   c. Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.
7. Define the following and give an example of each: **Check Answer:** [4]
   a. dispersion force
   b. dipole-dipole attraction
   c. hydrogen bond
8. The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?
9. Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe? **Check Answer:** [5]

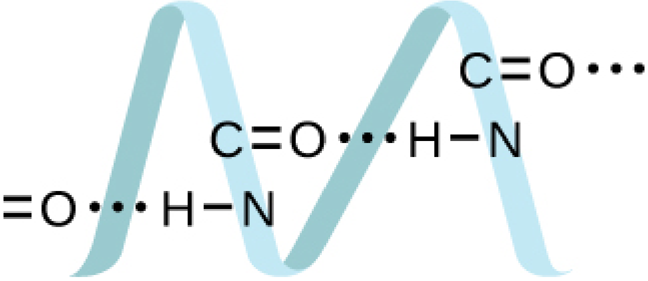
10. Neon and HF have approximately the same molecular masses.
    a. Explain why the boiling points of Neon and HF differ.
    b. Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.
11. Arrange each of the following sets of compounds in order of increasing boiling point temperature: **Check Answer:** [6]
    a. HCl, H_2O, SiH_4
    b. F_2, Cl_2, Br_2
    c. CH_4, C_2H_6, C_3H_8
    d. O_2, NO, N_2
12. The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.
13. On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses. **Check Answer:** [7]
14. On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.
15. The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer. **Check Answer:** [8]
16. Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?
17. Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules. **Check Answer:** [9]
18. Under certain conditions, molecules of acetic acid, CH_3COOH (shown below), form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:



Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

19. Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix.

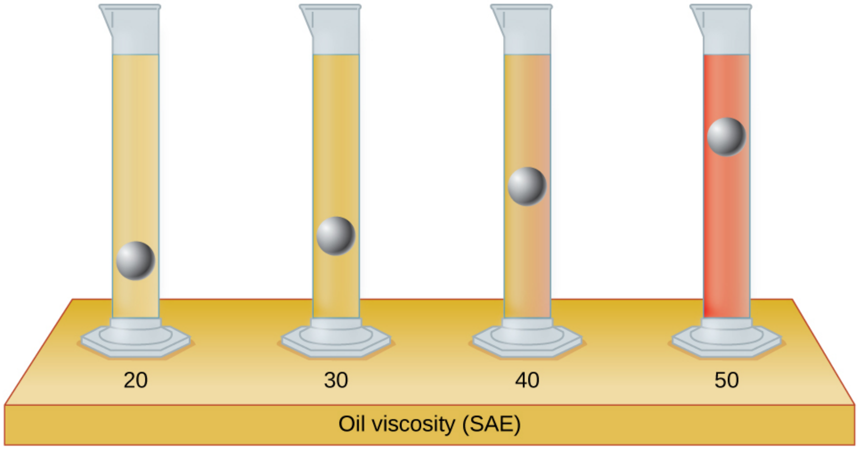
What kind of IMF is responsible for holding the protein strand in this shape? On the protein image below, show the locations of the IMFs that hold the protein together: **Check Answer:** [10]



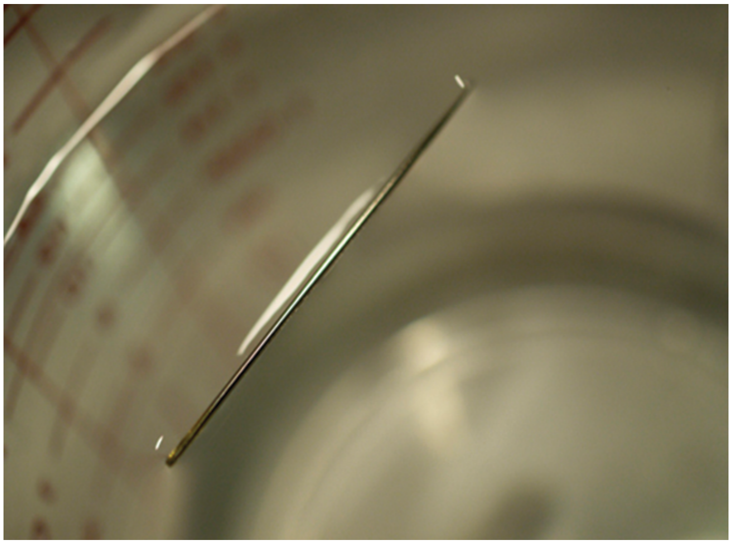
20. The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.
21. Identify the intermolecular forces present in the following solids: **Check Answer:** [11]
    a. CH_3CH_2OH
    b. $CH_3CH_2CH_3$
    c. CH_3CH_2Cl

13.2 – Properties of Liquids

1. The test tubes shown below contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration. Rank the motor oils in order of increasing viscosity, and explain your reasoning:

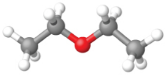
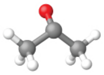
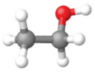
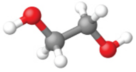


2. Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. See figure below. Explain at a molecular level how this is possible: **Check Answer:** [12]



(credit: Cory Zanker)

3. The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown in the figure below.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

   a. Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.
   b. Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

4. You may have heard someone use the figure of speech "slower than molasses in winter" to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature. **Check Answer:** [13]
5. It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.
6. The surface tension and viscosity of water at several different temperatures are given in the data table below. **Check Answer:** [14]

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

   a. As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
   b. As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
7. At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to Example 13.2a for the required information.
8. Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube? **Check Answer:** [15]

13.3 – Phase Transitions

1. Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?
2. Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change? **Check Answer:** [16]
3. What feature characterizes the dynamic equilibrium between a liquid and its vapour in a closed container?
4. Identify two common observations indicating some liquids have sufficient vapour pressures to noticeably evaporate? **Check Answer:** [17]
5. Identify two common observations indicating some solids, such as dry ice and mothballs, have vapour pressures sufficient to sublime?
6. What is the relationship between the intermolecular forces in a liquid and its vapour pressure? **Check Answer:** [18]
7. What is the relationship between the intermolecular forces in a solid and its melting temperature?
8. Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day? **Check Answer:** [19]
9. Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapour pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.
10. When is the boiling point of a liquid equal to its normal boiling point? **Check Answer:** [20]
11. How does the boiling of a liquid differ from its evaporation?

12. Use the information in Figure 13.3d to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa. **Check Answer:** [21]
13. A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapour. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapour, what would be the approximate pressure of the vapour produced?
14. Explain the following observations:
    a. It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).
    b. Perspiring is a mechanism for cooling the body. **Check Answer:** [22]
15. The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.
16. Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though the type of IMF (dispersion) is the same. **Check Answer:** [23]
17. Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.
18. The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or −8.4 kJ/mol? Discuss the plausibility of each of these answers. **Check Answer:** [24]
19. The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.
20. Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride. **Check Answer:** [25]
21. Which contains the compounds listed correctly in order of increasing boiling points?
    a. $N_2 < CS_2 < H_2O < KCl$
    b. $H_2O < N_2 < CS_2 < KCl$
    c. $N_2 < KCl < CS_2 < H_2O$
    d. $CS_2 < N_2 < KCl < H_2O$
    e. $KCl < H_2O < CS_2 < N_2$
22. How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C? **Check Answer:** [26]
23. Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapour? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)
24. Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a ΔH_{fusion} = 9.37 kJ/mol.

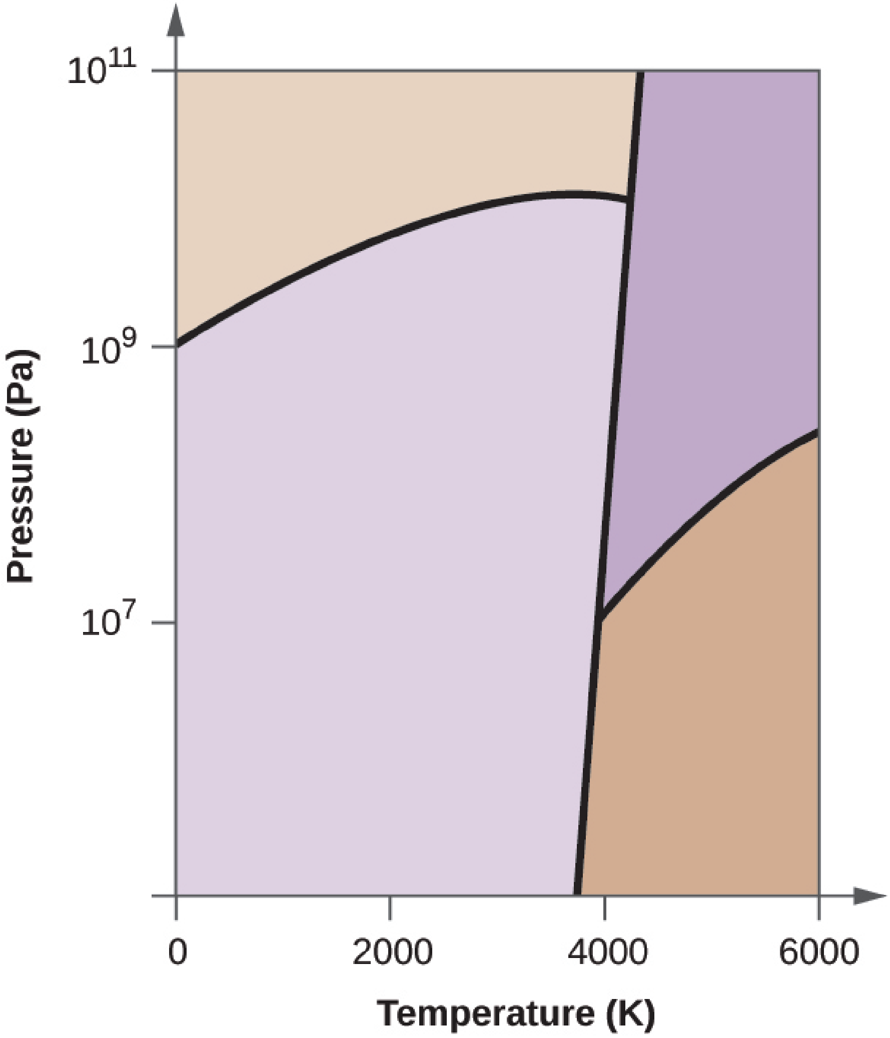
   a. How much energy is required to melt 263.1 g $TiCl_4$?
   b. For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{\text{vaporization}}$? Explain your reasoning. **Check Answer:** [27]

13.4 – Phase Diagrams

1. From the phase diagram for water (Figure 13.4b), determine the state of water at:
   a. 35 °C and 85 kPa
   b. −15 °C and 40 kPa
   c. −15 °C and 0.1 kPa
   d. 75 °C and 3 kPa
   e. 40 °C and 0.1 kPa
   f. 60 °C and 50 kPa
2. What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C? **Check Answer:** [28]
3. Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.
4. From the phase diagram for carbon dioxide in Figure 13.4e, determine the state of CO_2 at:
   a. 20 °C and 1000 kPa
   b. 10 °C and 2000 kPa
   c. 10 °C and 100 kPa
   d. −40 °C and 500 kPa
   e. −80 °C and 1500 kPa
   f. −80 °C and 10 kPa **Check Answer:** [29]
5. Determine the phase changes that carbon dioxide undergoes as the pressure changes if the temperature is held at −50 °C? If the temperature is held at −40 °C? At 20 °C? (See the phase diagram in Figure 13.4e.)
6. Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature. **Check Answer:** [30]
7. Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See Figure 13.4e for the phase diagram.)
8. If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on

the line. If it does not snow, will they dry anyway? Explain your answer. **Check Answer:** [31]

9. Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.
10. Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the phase diagram below:



   a. On the phase diagram, label the gas and liquid regions.
   b. Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
   c. If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.
   d. Circle each triple point on the phase diagram.
   e. In what phase does carbon exist at 5000 K and 10^8 Pa?
   f. If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any? **Check Answer:** [32]

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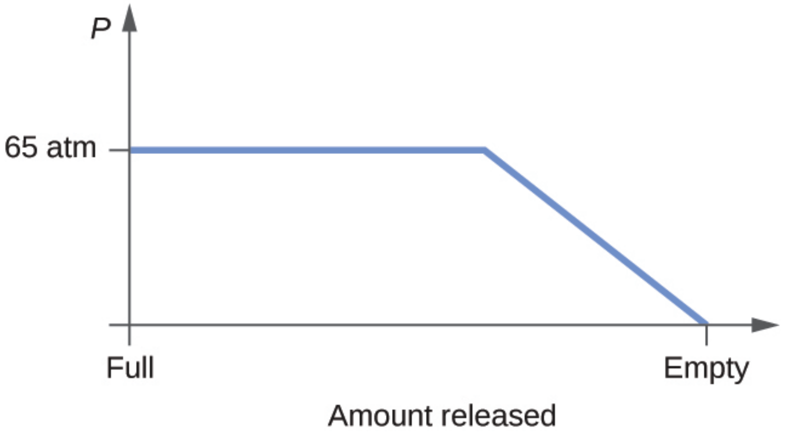
Notes

1. Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.
2. They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.
3. All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.
4. (a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICI molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: $\mathrm{HF}\cdots\mathrm{HF}$).
5. The London forces typically increase as the number of electrons increase.
6. (a) $SiH_4 < HCl < H_2O$; (b) $F_2 < Cl_2 < Br_2$; (c) $CH_4 < C_2H_6 < C_3H_8$; (d) $N_2 < O_2 < NO$
7. Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.
8. −85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.
9. The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.
10. H-bonding is the principle IMF holding the DNA strands together. The H-bonding is between the $\mathrm{N-H}$ and

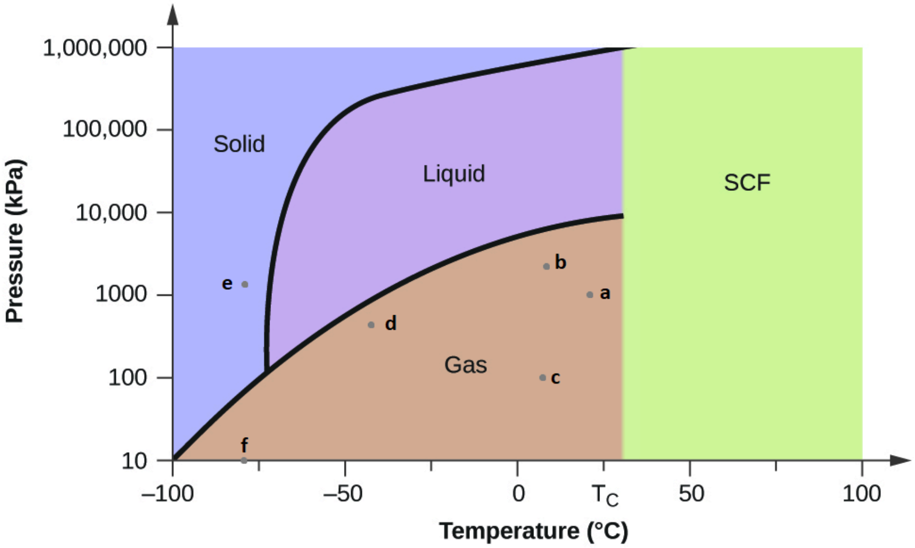
$C = O$.

11. (a) hydrogen bonding and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces
12. The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of "skin" at its surface. This skin can support a bug or paper clip if gently placed on the water.
13. Temperature has an effect on intermolecular forces: the higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid; the lower the temperature, the lesser the intermolecular forces are overcome, and so the less viscous the liquid.
14. (a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.
15. 9.5×10^{-5} m
16. The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.
17. We can see the amount of liquid in an open container decrease and we can smell the vapour of some liquids.
18. The vapour pressure of a liquid decreases as the strength of its intermolecular forces increases.
19. As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.
20. When the pressure of gas above the liquid is exactly 1 atm
21. approximately 95 °C
22. (a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapour than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.
23. Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.
24. The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of −8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.
25. The thermal energy (heat) needed to evaporate the liquid is removed from the skin.
26. 1130 kJ
27. (a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.
28. At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapour; at pressures higher than about 75 torr, it converts into a liquid. At −40 °C, water goes from a gas to a solid as the pressure increases above very low values.
29. (a) liquid; (b) solid; (c) gas; (d) gas; (e) gas; (f) gas



30.

31. Yes, ice will sublime, although it may take it several days. Ice has a small vapour pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.



32.

CHAPTER 14: SOLUTIONS

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- What a solution is, how they form, their molecular properties, and how they can either absorb or produce heat
- The effects that temperature and pressure have on solubility
- Solution concentration calculations using the molarity equation, dilution calculations using

the dilution equation, and the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- The effect of solute concentration on various solution properties such as vapour pressure, boiling point, freezing point, and osmotic pressure
- The process of distillation and its practical applications
- The process of osmosis and how it is applied industrially and in nature
- The composition and properties of colloidal dispersions, and applications of colloids

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Mathematical measurements, uncertainty, accuracy, and precision
- The periodic table, molecular formulas, and the difference between elements and compounds
- Nomenclature of molecular and ionic compounds, and acids
- The concept of the mole, molecular mass, and Avogadro's number
- Writing and balancing chemical equations
- Stoichiometry

Figure 14a Coral reefs, such as this one at the Palmyra Atoll National Wildlife Refuge, are vital to the ecosystem of earth's oceans but are threatened by climate change and dissolved pollution. Marine life depends on the specific chemical composition of the complex mixture we know as seawater. (credit: modification of work by Jim Maragos/USFWS – Pacific Region, CC BY-NC 2.0. / Cropped.)

Coral reefs are home to about 25% of all marine species. They are being threatened by climate change, oceanic acidification, and water pollution, all of which change the composition of the solution we know as seawater. Dissolved oxygen in seawater is critical for sea creatures, but as the oceans warm, oxygen becomes less soluble. As the concentration of carbon dioxide in the atmosphere increases, the concentration of carbon dioxide in the oceans increases, contributing to oceanic acidification. Coral reefs are particularly sensitive to the acidification of the ocean, since the exoskeletons of the coral polyps are soluble in acidic solutions. Humans contribute to the changing of seawater composition by allowing agricultural runoff and other forms of pollution to affect our oceans.

Solutions are crucial to the processes that sustain life and to many other processes involving chemical reactions. In this chapter, we will consider the nature of solutions, and examine factors that determine whether a solution will form and what properties it may have. In addition, we will discuss colloids—systems that resemble solutions but consist of dispersions of particles somewhat larger than ordinary molecules or ions.

Attribution & References

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14.1 SOLUTIONS: AN INTRODUCTION

Learning Objectives

By the end of this section, you will be able to:

- Describe the basic properties of solutions and how they form
- Predict whether a given mixture will yield a solution based on molecular properties of its components
- Explain why some solutions either produce or absorb heat when they form

An earlier chapter of this text introduced **solutions**, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the **solvent**. The other components of the solution present in relatively lesser concentrations are called **solutes**. Sugar is a covalent solid composed of sucrose molecules, $C_{12}H_{22}O_{11}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

$$\mathrm{C_{12}H_{22}O_{11}}(s) \longrightarrow \mathrm{C_{12}H_{22}O_{11}}(aq)$$

The subscript "*aq*" in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to "settle out" over time.

Potassium dichromate, $K_2Cr_2O_7$, is an ionic compound composed of colourless potassium ions, K^+, and orange dichromate ions, $\mathrm{Cr_2O_7}^{2-}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (Figure 14.1a), as indicated in this equation:

$$\mathrm{K_2Cr_2O_7}(s) \longrightarrow 2\mathrm{K^+}(aq) + \mathrm{Cr_2O_7}^{2-}(aq)$$

As for the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.

Figure 14.1a When potassium dichromate ($K_2Cr_2O_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 14.1a

Practice using the following PhET simulation: Sugar and Salt Solutions

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many **alloys** are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. Table 14.1a gives examples of several different solutions and the phases of the solutes and solvents.

Table 14.1a Different Types of Solutions

Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks[1]	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Solutions exhibit these defining traits:

- They are homogeneous; that is, after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).

- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in Table 14.1a.
- The components of a solution are dispersed on a molecular scale; that is, they consist of a mixture of separated molecules, atoms, and/or ions.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously, within limits.

The Formation of Solutions

The formation of a solution is an example of a **spontaneous process**, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes we stir a mixture to speed up the dissolution process, but this is not necessary; a homogeneous solution would form if we waited long enough. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favour*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increase in the disorder in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in disorder always results when a solution forms.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an **ideal solution**. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behaviour) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution (Figure 14.1b). The formation of this solution clearly involves an increase in disorder, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

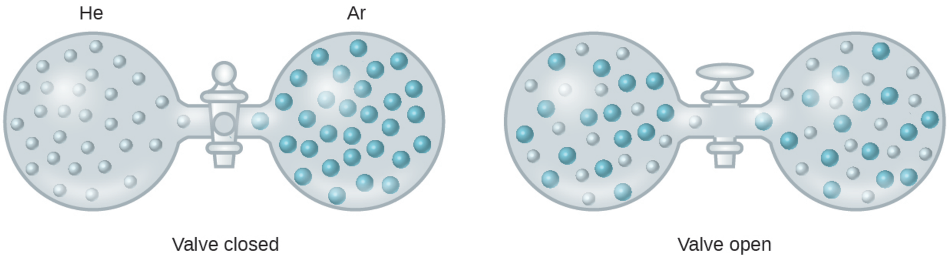

Figure 14.1b Samples of helium and argon spontaneously mix to give a solution in which the disorder of the atoms of the two gases is increased (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol (C_2H_5OH) form ideal solutions, as do mixtures of the hydrocarbons pentane, C_5H_{12}, and hexane, C_6H_{14}. Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in Figure 14.1b will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how diffusion alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of intermolecular forces of attraction between solute and solvent species may prevent dissolution.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in Figure 14.1c, the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as **solvation**). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.

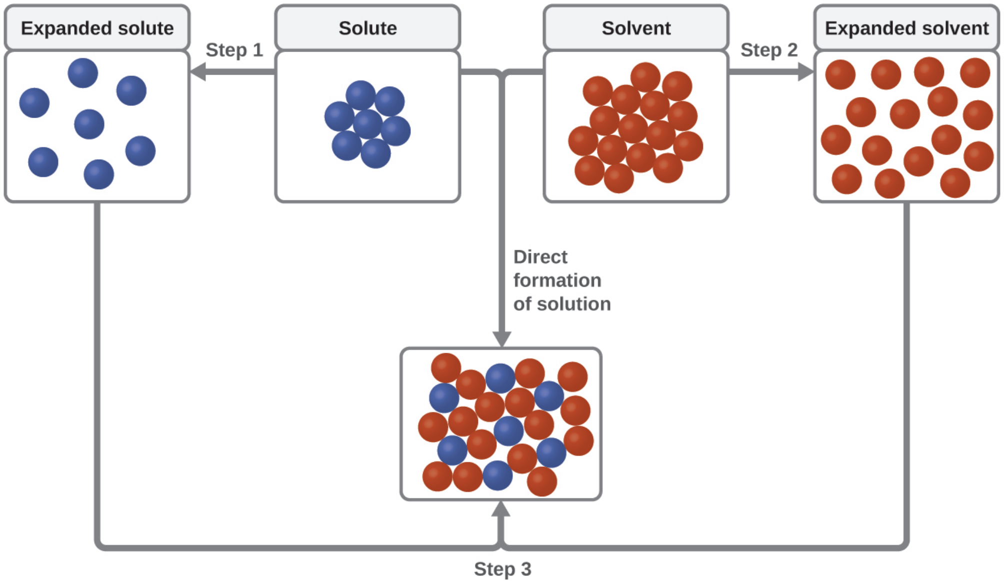

Figure 14.1c This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

For example, cooking oils and water will not mix to any appreciable extent to yield solutions (Figure 14.1d). Hydrogen bonding is the dominant intermolecular attractive force present in liquid water; the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.

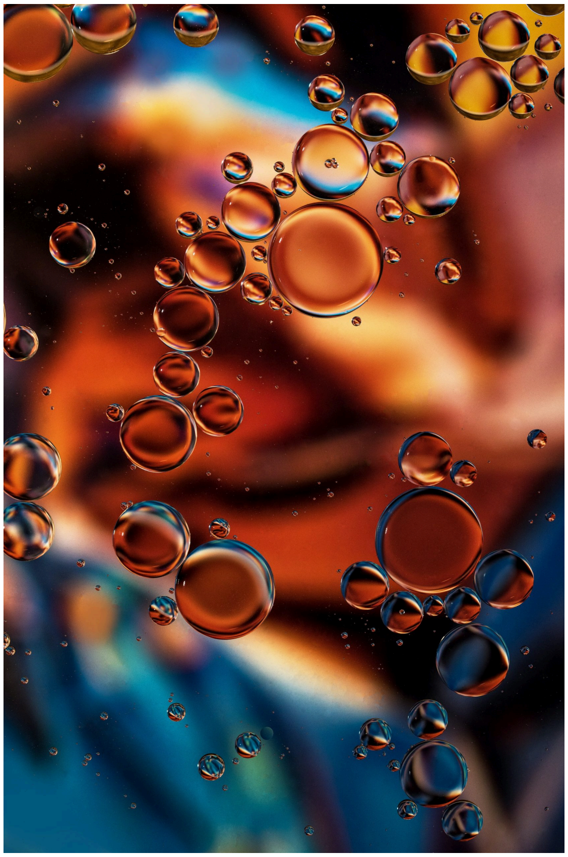

Figure 14.1d A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: work by David Clode, Unsplash license).

On the other hand, a mixture of ethanol and water will mix in any proportion to yield a solution. In this case, both substances are capable of hydrogen bonding, and so the solvation process is sufficiently exothermic to compensate for the endothermic separations of solute and solvent molecules.

As noted at the beginning of this module, spontaneous solution formation is favoured, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs for treating injuries like the one pictured in Figure 14.1e. A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3. When the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.

Figure 14.1e An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch Comparing Temperature Change from Heat of Solution (KCl vs NaOH) (2 mins)

Indigenous Perspective: Maple Syrup

Figure 14.1f Sap collection (credit: work by Oven Fresh, PD)

For thousands of years maple syrup has been gathered from maple trees in Canada and the northern United States, a practice that has sustained Indigenous communities while also helping to connect them to the land. This is a practice carried out by the Anishinaabeg, Haudenosaunee and other First Nations. The physical and chemical properties of this unique solution give it the ability to act as not only a sweetener, but also as an anesthetic and a desiccant to help cure meats. Aside from containing many nutrients and carbohydrates, maple syrup was also used as an essential trade item. To learn more about the chemistry of maple syrup and its importance in Indigenous culture, please visit:

- The Indigenous Origins of Maple Syrup [New Tab]
- Food for Thought: The rich Indigenous history of maple syrup [New Tab]

Attribution & References

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Notes

1. If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.

14.2 SOLUBILITY

Learning Objectives

By the end of this section, you will be able to:

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous module of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The concentration of salt in the solution at this point is known as its solubility.

The **solubility** of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*. Referring to the example of salt in water:

$$\mathrm{NaCl}(s) \leftrightharpoons \mathrm{Na}^{+}(aq) \ + \ \mathrm{Cl}^{-}(aq)$$

When a solute's concentration is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute's concentration is less than its solubility, the solution is said to be **unsaturated**. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

If we add more salt to a saturated solution of salt, we see it fall to the bottom and no more seems to dissolve. In fact, the added salt does dissolve, as represented by the forward direction of the dissolution equation. Accompanying this process, dissolved salt will precipitate, as depicted by the reverse direction of the equation. The system is said to be at equilibrium when these two reciprocal processes are occurring at equal rates, and so the amount of undissolved and dissolved salt remains constant. Support for the simultaneous occurrence of the dissolution and precipitation processes is provided by noting that the number and sizes of the undissolved salt crystals will change over time, though their combined mass will remain the same.

Exercise 14.2a

Practice using the following PhET simulation: Salts & Solubility

Solutions in which a solute concentration *exceeds* its solubility may be prepared. Such solutions are said to be **supersaturated**, and they are interesting examples of *nonequilibrium* states. For example, the carbonated beverage in an open container that has not yet “gone flat” is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its equilibrium value.

Watch Crystal Growing – Cool Science Experiment (3 mins)

Watch crystallization of sodium acetate (v2) (2 min)

Solutions of Gases in Liquids

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent’s chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure 14.2a). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

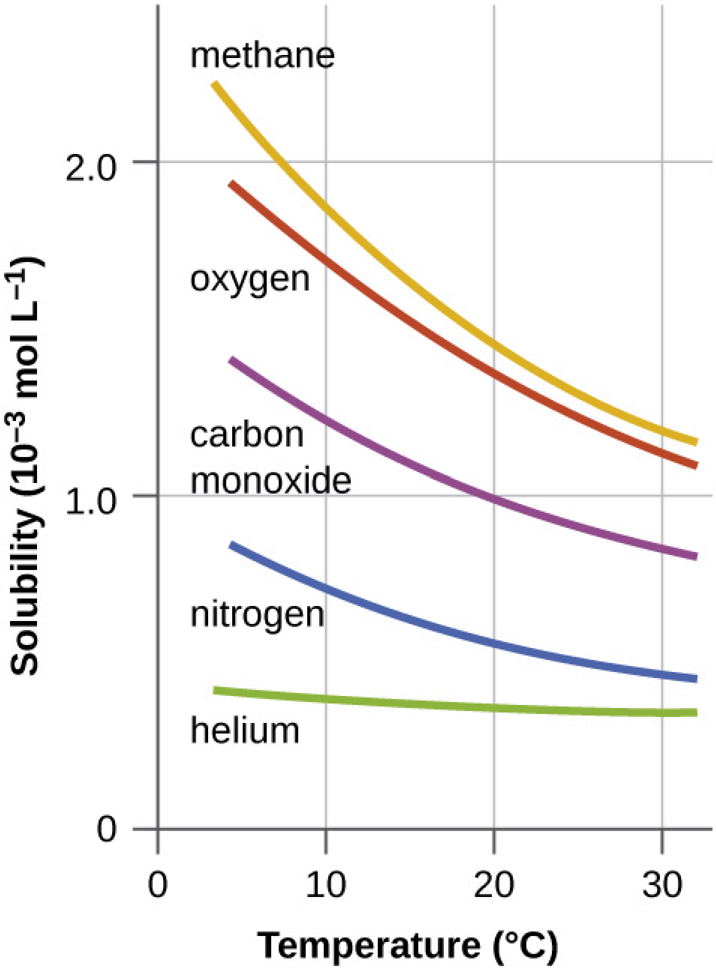

Figure 14.2a The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure 14.2b).

(a) (b)

Figure 14.2b (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West, CC BY 2.0; credit b: modification of work by U.S. Fish and Wildlife Service, PD)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 14.2c). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

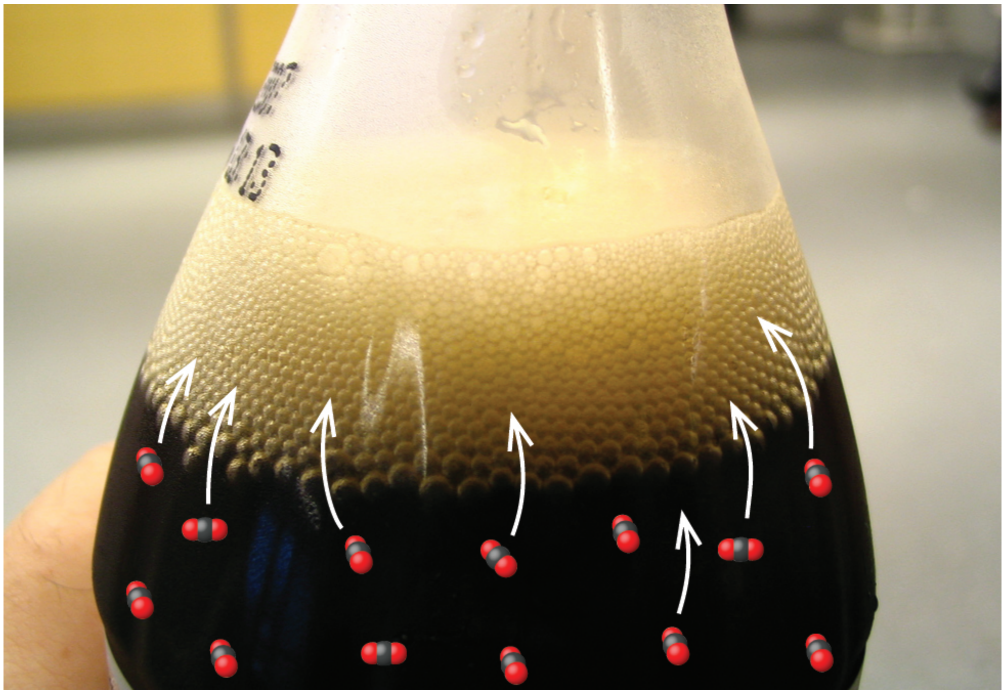

Figure 14.2c Opening the bottle of carbonated beverage reduces the pressure of the *gaseous* carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some *dissolved* carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Chiara Coetzee, CC0; in *Chemistry (OpenStax)*, CC BY 4.0).

For many gaseous solutes, the relationship between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_\text{g} = kP_\text{g}$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of **Henry's law**: The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.

Example 14.2a

Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for *k*.

$$\begin{aligned} C_{\text{g}} &= kP_{\text{g}} \\ k &= \frac{C_{\text{g}}}{P_{\text{g}}} \\ &= \frac{1.38 \times 10^{-3} \text{ mol L}^{-1}}{101.3 \text{ kPa}} \\ &= 1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1} \\ &= (1.82 \times 10^{-6} \text{ mol L}^{-1} \text{ torr}^{-1}) \end{aligned}$$

Now we can use *k* to find the solubility at the lower pressure.

$$C_{\text{g}} = kP_{\text{g}}$$
$$= 1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1} \times 20.7 \text{ kPa}$$
$$(\text{or } 1.82 \times 10^{-6} \text{ mol L}^{-1} \text{ torr}^{-1} \times 155 \text{ torr})$$
$$= 2.82 \times 10^{-4} \text{ mol L}^{-1}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 14.2b

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Check Your Answer[1]

Decompression Sickness or "The Bends"

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 14.2d).

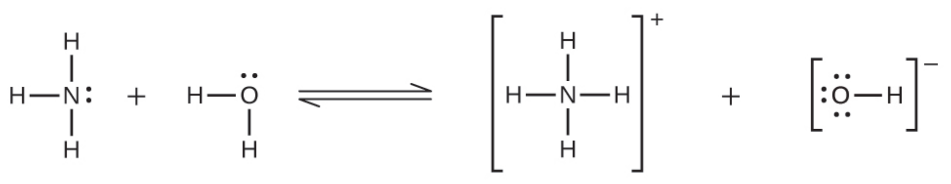

Figure 14.2d Reaction of ammonia with water to form ammonium ion and hydroxide ion (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be **miscible**. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in Figure 14.2e) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.

Figure 14.2e Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: work by dno1967, CC BY 2.0)

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom "like dissolves like."

Two liquids that do not mix to an appreciable extent are called **immiscible**. Layers are formed when we pour immiscible liquids into the same container. Gasoline, oil (Figure 14.2f), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.

Figure 14.2f Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: work by Yortw, CC BY 2.0)

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be **partially miscible**. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discoloured by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark colour of the bromine layer (Figure 14.2g).

Figure 14.2g Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers in *Chemistry (OpenStax)*, CC BY 4.0).

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of inorganic solids in water is shown by the solubility curves in Figure 14.2h. Reviewing these data indicate a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.

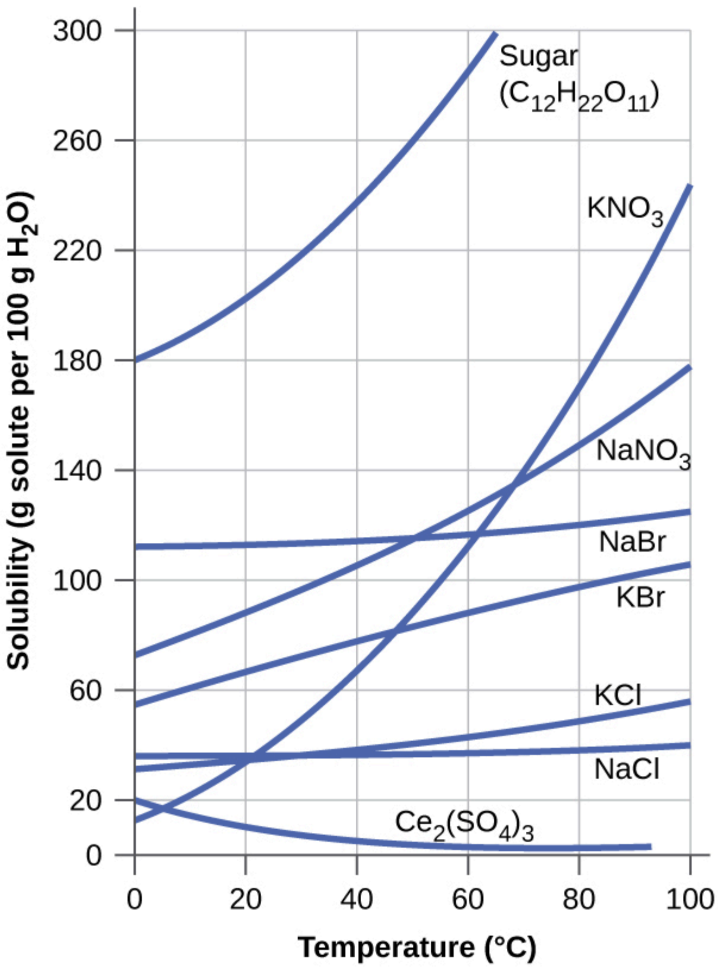

Figure 14.2h This graph shows how the solubility of several solids changes with temperature (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers take advantage of this behaviour.

Watch Crystallization of the "Magic" Gel Hand Warmer bag (HD) (1 min)

Solubility of Ionic Compounds

The solubility of ionic compounds can be predicted based on the nature of the cations and anions present in the compound. Compounds that are soluble (along with their exceptions) can be seen in Table 14.2a, while those that are insoluble (along with their exceptions) can be seen in Table 14.2b.

Table 14.2a Soluble Ionic Compounds

Compounds containing these ions	**Exceptions**
NH_4^+	none
Li^+	none
Na^+	none
K^+	none
Rb^+	none
Cs^+	none
Cl^-	Compounds with Ag+, Hg_2^{2+}, Pb^{2+}
Br^-	Compounds with Ag+, Hg_2^{2+}, Pb^{2+}
I^-	Compounds with Ag+, Hg_2^{2+}, Pb^{2+}
F^-	Compounds with group 2 metal cations Pb^{2+}, Fe^{2+}
$C_2H_3O_2^-$	None
HCO_3^-	None
CIO_3^-	None
SO_4^{2-}	Compounds with Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+}, Sr^{2+}

Source: "Table 14.2a" by Gregory Anderson is adapted from "4.2 Classifying Chemical Reactions" in *Chemistry (OpenStax)*, CC BY 4.0

Table 14.2b Insoluble Ionic Compounds

Compounds containing these ions	Exceptions
CO_3^{2-}	Compounds with group 1 cations and NH_4^+
CrO_4^{2-}	Compounds with group 1 cations and NH_4^+
PO_4^{3-}	Compounds with group 1 cations and NH_4^+
S^{2-}	Compounds with group 1 cations and NH_4^+
OH^-	Compounds with group 1 cations and Ba^{2+}

Source: "Table 14.2b" by Gregory Anderson is adapted from "4.2 Classifying Chemical Reactions" in *Chemistry (OpenStax)*, CC BY 4.0

Links to Interactive Learning Tools

Explore Precipitation Reactions from the Physics Classroom.

Practice Solution Word Definitions from eCampusOntario H5P Studio.

Key Equations

- $C_g = kP_g$

Attribution & References

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Notes

1. 7.25×10^{-3} in 100.0 mL or 0.0725 g/L

14.3 MOLARITY

Learning Objectives

By the end of this section, you will be able to:

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (see Figure 14.3a). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.

Figure 14.3a Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Photo by Jane Whitney in *Chemistry (OpenStax)*, CC BY 4.0).

Solutions

We have previously defined solutions as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce some of the basic properties of solutions.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the **solvent** and may be viewed as the medium in which the other components are dispersed, or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an **aqueous solution**.

A **solute** is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity (*M*)** is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 litre (1 L) of the solution:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Example 14.3a

Calculating Molarity

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133 \text{ mol}}{355 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.375\ M$$

Exercise 14.3a

Check Your Learning Exercise (Text Version)
A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

a. 0.05 M
b. 0.03 M
c. 0.07 M
d. 0.04 M

Check Your Answer[1]

Source: "Exercise 14.3a" is adapted from "Example 6.3-1" in General Chemistry 1 & 2, a derivative of

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Example 14.3b

Deriving Moles and Volumes from Molarity

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 14.3a?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in Example 14.3a, 0.375 *M*:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 0.375\,\frac{\text{mol sugar}}{\text{L}} \times (10\text{ mL} \times \frac{1\text{L}}{1000\text{ mL}}) = 0.004\text{ mol sugar}$$

Exercise 14.3b

Check Your Learning Exercise (Text Version)
What volume (mL) of the sweetened tea (0.05*M*) described in Exercise 14.3a contains the same amount of sugar as 10 mL of the soft drink described in Example 14.3b?

a. 80 mL
b. 75 mL
c. 70 mL
d. 85 mL

Check Your Answer[2]

Source: "Exercise 14.3b" is adapted from "Example 6.3-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 14.3c

Calculating Molarity from the Mass of Solute

Distilled white vinegar (Figure 14.3b) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?

Figure 14.3b: Distilled white vinegar is a solution of acetic acid in water. (credit: modification of work by HomeSpot HQ, CC BY 2.0)

Solution

As in previous textbox shaded, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute's molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\text{ g }\mathrm{CH_3CO_2H} \times \frac{1\ \text{mol}\ \mathrm{CH_2CO_2H}}{60.052\ \text{g}\ \mathrm{CH_2CO_2H}}}{0.500\text{ L solution}} = 0.839\ M$$

$$M \quad = \frac{\text{mol solute}}{\text{L solution}} = 0.839\ M$$

$$M \quad = \frac{0.839\ \text{mol solute}}{1.00\ \text{L solution}}$$

Exercise 14.3c

Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Check Your Answer[3]

Example 14.3d

Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in 14.2b:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$
$$\text{mol solute} = M \times \text{L solution}$$
$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}} \times 0.250\ \text{L} = 1.325\ \text{mol NaCl}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325\ \text{mol NaCl} \times \frac{58.44\ \text{g NaCl}}{\text{mol NaCl}} = 77.4\ \text{g NaCl}$$

Exercise 14.3d

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-*M* solution of calcium chloride?

Check Your Answer[4]

When performing stepwise calculations, as in Example 4, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example 4, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (see Example 14.3e). This eliminates intermediate steps so that only the final result is rounded.

Example 14.3e

Determining the Volume of Solution Containing a Given Mass of Solute

In Example 14.3c, we found the typical concentration of vinegar to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

$$75.6\ \text{g}\ CH_3CO_2H(\frac{\text{mol}\ CH_3CO_2H}{60.05\ \text{g}})(\frac{\text{L solution}}{0.839\ \text{mol}\ CH_3CO_2H}) = 1.50\ \text{L solution}$$

Exercise 14.3e

Check Your Learning Exercise (Text Version)
What volume of a 1.50-M KBr solution contains 66.0 g KBr?

a. 0.370 L
b. 0.250 L
c. 0.983 L
d. 0.137 L

Check Your Answer[5]

Source: "Exercise 14.3e" is adapted from "Example 6.3-5" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 14.3c).

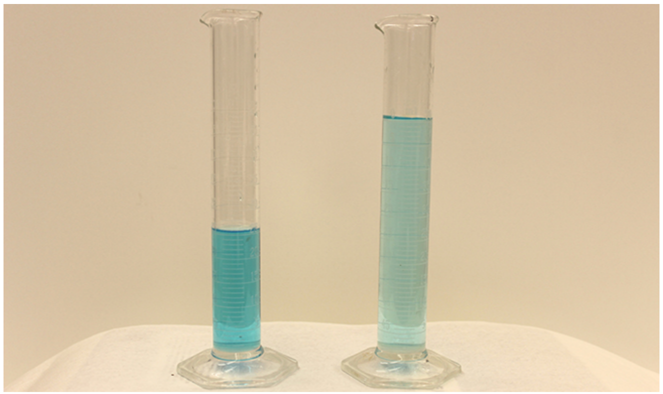

Figure 14.3c Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, we can achieve a particular concentration. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents (Figure 14.3d).

Figure 14.3d A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of $KMnO_4$ in a flask. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the molar amount of solute in a solution is equal to the product of the solution's molarity and its volume in litres:

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1 L_1$$

$$n_2 = M_2L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution,*$n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1L_1 = M_2L_2$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and litres as the unit of volume, other units of concentration and volume may be used, so long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1V_1 = C_2V_2$$

where *C* and *V* are concentration and volume, respectively.

Exercise 14.3f

Practice using the following PhET simulation: Concentration.

Exercise 14.3g

Practice using the following PhET simulation: Molarity

Example 14.3f

Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-*M* solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

$$\begin{aligned} C_1V_1 &= C_2V_2 \\ C_2 &= \frac{C_1V_1}{V_2} \end{aligned}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution's concentration to be less than one-half 5 *M*. We will compare this ballpark estimate to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850\ \text{L} \times 5.00\frac{\text{mol}}{\text{L}}}{1.80\ \text{L}} = 2.36\ M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 *M*).

Exercise 14.3h

Check Your Learning Exercise (Text Version)
What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH_3OH to 500.0 mL?

a. 0.102 *M* CH_3OH
b. 0.202 *M* CH_3OH
c. 0.205 *M* CH_3OH
d. 0.703 *M* CH_3OH

Check Your Answer[6]

Source: "Exercise 14.3h" is adapted from "Example 6.3-6" in General Chemistry 1 & 2, a derivative of

Example 14.3g

Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

$$\begin{aligned} C_1V_1 &= C_2V_2 \\ V_2 &= \frac{C_1V_1}{C_2} \end{aligned}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), we would expect the volume of the diluted solution to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$\begin{aligned} V_2 &= \frac{(0.45\ M)(0.011\ \text{L})}{0.12\ M} \\ V_2 &= 0.041\ \text{L} \end{aligned}$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

Exercise 14.3i

A laboratory experiment calls for 0.125 *M* HNO_3. What volume of 0.125 *M* HNO_3 can be prepared from 0.250 L of 1.88 *M* HNO_3?

Check Your Answer[7]

Example 14.3h

Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:

$$C_1V_1 = C_2V_2$$
$$V_2 = \frac{C_2V_2}{C_2}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 litres. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\ M)(5.00\ \text{L})}{1.59\ M}$$
$$V_1 = 0.314\ \text{L}$$

Thus, we would need 0.314 L of the 1.59-*M* solution to prepare the desired solution. This result is consistent with our rough estimate.

Exercise 14.3j

What volume of a 0.575-*M* solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

Check Your Answer[8]

Visualizing Different Solutes in Solution

When seeking to understand compounds in solution, we must differentiate between the behaviour of covalent compounds and ionic compounds. Assuming the solid dissolves, ionic compounds will dissociate into their ions. In contrast, for covalent compounds, the molecules of the compound remain intact.

So far in this section, we have been examining solutions of sugar ($C_6H_{12}O_6$). If we were to be able to see on the level of molecules, we might see a solution like that below (figure 14.3e), where a triangle represents a molecule of glucose. While the molecules move around in the solution once they are dissolved in water, the atoms in the molecule do not break apart. The covalent bonds are intact.

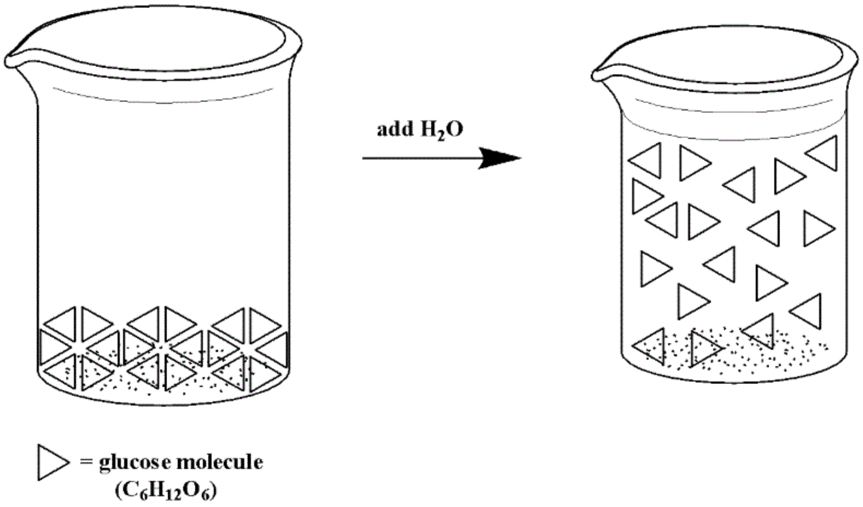

Figure 14.3e Glucose, when placed into a solvent such as water, does not dissociate. The molecules maintain their covalent bonds, and thus float around in solution as complete glucose molecules (triangles above) (*General Chemistry I & II*, CC BY 4.0)

In contrast, when an ionic compound dissolves in solution, the cations and anions are separated (they dissociate) and each ion is surrounded by water molecules. We can depict the dissociation process for a compound like NaCl using the image below (figure 14.3f):

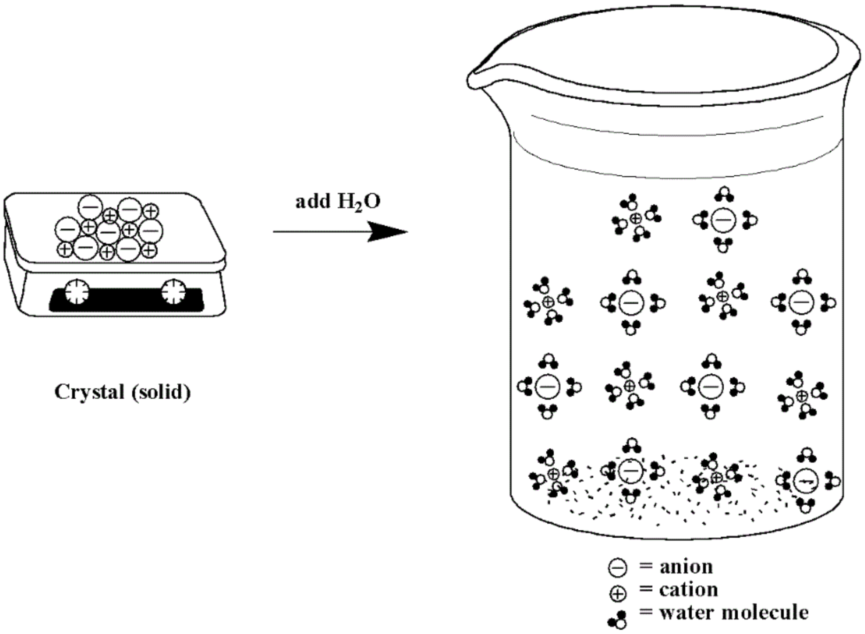

Figure 14.3f Ionic solids, when placed into a polar solvent such as water, will undergo dissociation. Each ion is surrounded by water molecules due to dipole-dipole interactions, thus pulling the ionic compound apart into individual ions (*General Chemistry I & II*, CC BY 4.0)

If we leave out the water molecules (to make it easier to see the ions) below is an example of a sodium sulfate, Na_2SO_4, solution. The sulfate anions will have a -2 charge and the sodium cations will have a +1 charge.

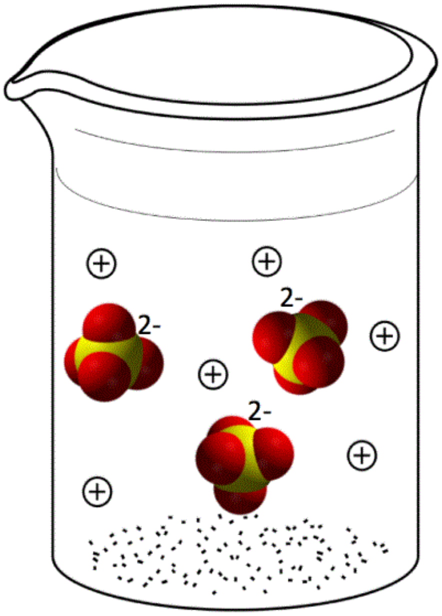

Figure 14.3g: Sodium sulfate (Na_2SO_4), when placed into a polar solvent such as water, will dissociate into individual Na^+ ions and SO_4^{2-} ions (*General Chemistry I & II*, CC BY 4.0)

Note that when the ionic compound dissociates, the covalent bonds of any polyatomic ions (like sulfate) remain intact. Also note that the ions in solution are present in the same ratio as in the solid compound. In this case, there are 2 Na^+ ions for every 1 SO_4^{2-} ion.

Example 14.3h

Determining Moles of Ions in Ionic Compounds:

For each of the following, if 1 mole of the compound were to dissolve and dissociate, how many moles of ions would be present in:

a. magnesium chloride?
b. ammonium phosphate?

Solution:

a. The formula for magnesium chloride is $MgCl_2$. It is made of Mg^{2+} ions and Cl^- ions. If a mole of $MgCl_2$ dissociates in solution, we'll get 1 mole of Mg^{2+} ions and 2 moles of Cl^- ions, for a total of 3 moles of ions.

b. The formula for ammonium phosphate is $(NH_4)_3PO_4$. It is made of NH_4^+ ions and PO_4^{3-} ions. If a mole of $(NH_4)_3PO_4$ dissociates in solution, we'll get 3 moles of NH_4^+ ions and 1 mole of PO_4^{3-} ions, for a total of 4 moles of ions.

Exercise 14.3k

How many moles of *each* ion will be produced from 1 mole of ammonium sulfate?

Check Your Answer[9]

Because an ionic compound dissociates in solution, we can use our knowledge of molarity to describe the concentration of the compound in solution, OR the concentration of ions in solution.

Example 14.3i

Relating Concentrations of a Compound with Concentrations of its Ions in Solution

If you have a solution that is 0.5 M potassium sulfate, what is the concentration of potassium ions in solution? of sulfate ions in solution?

Solution

To answer the questions above, we want to know how many moles of each ion are present in a litre of solution. We are given that the solution is 0.5 M K_2SO_4. Given the definition of molarity, we can express the following:

$$0.5 \text{ M } \mathrm{K_2SO_4} = \frac{0.5 \text{ mol } \mathrm{K_2SO_4}}{1 \text{ L}}$$

We can then use the appropriate relationship we know from the formula of potassium sulfate to make the appropriate conversions:

$$\frac{0.5\text{ mol K}_2\text{SO}_4}{1\text{ L}} \times \frac{2\text{ mol K}^+}{1\text{ mol K}_2\text{SO}_4} = \frac{1\text{ mol K}^+}{1\text{ L}} = 1\text{ M K}^+$$

$$\frac{0.5\text{ mol K}_2\text{SO}_4}{1\text{ L}} \times \frac{1\text{ mol SO}_4^{2-}}{1\text{ mol K}_2\text{SO}_4} = \frac{0.5\text{ mol SO}_4^{2-}}{1\text{ L}} = 0.5\text{ M SO}_4^{2-}$$

Does this result make sense? We see that the concentration of potassium ions is twice that of the sulfate ions. Given that when the ions dissociate, there will be twice as many potassium ions present compared to sulfate ion, this result make sense.

Exercise 14.3l

If you have a 1.3 M solution of ammonium carbonate, $(NH_4)_2CO_3$, what is the concentration of each ion?

Check Your Answer[10]

Link to Interactive Learning Tools

Explore Dissociation from the Physics Classroom.

Explore Molarity Ranking Tasks from the Physics Classroom.

Explore Molarity Calculations from the Physics Classroom.

Key Equations

- $M = \dfrac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Attribution & References

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Notes

1. 0.05 M
2. 80 mL
3. 0.674 M
4. 5.55 g $CaCl_2$
5. 0.370 L
6. 0.102 M CH_3OH
7. 3.76 L
8. 0.261 L
9. 2 moles of NH_4^+, 1 mole of SO_4^{2-}
10. 2.6 M NH_4^+, 1.3 M CO_3^{2-}

14.4 OTHER UNITS FOR SOLUTION CONCENTRATIONS

Learning Objectives

By the end of this section, you will be able to:

- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- Perform computations relating a solution's concentration and its components' volumes and/or masses using these units

In the previous section, we introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. In this section, we will introduce some other units of concentration that are commonly used in various applications, either for convenience or by convention.

Mass Percentage

Earlier in this chapter, we introduced percent composition as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The **mass percentage** of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\%$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent.

Mass percentage is also referred to by similar names such as *percent mass, percent weight, weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle (Figure 14.4a) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.

Figure 14.4a Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 14.4a

Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

$$\%\ \text{glucose} = \frac{3.75\ \text{mg glucose} \times \frac{1\ \text{g}}{1000\ \text{mg}}}{5.0\ \text{spinal fluid}} = 0.075\%$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, we converted the units of solute in the numerator from mg to g to match the units in the denominator. We could just as easily have converted the denominator from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

Exercise 14.4a

A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?

Check Your Answer[1]

Example 14.4b

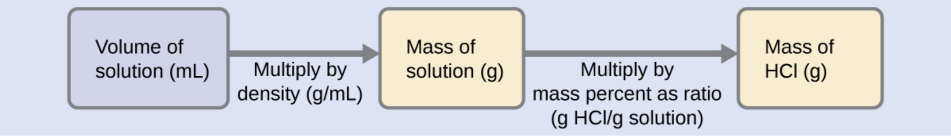
Calculations using Mass Percentage

"Concentrated" hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

Solution

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of

HCl. Since the solution density isn't greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or 5 ×× 40 = 200 g. In order to derive the mass of solute in a solution from its mass percentage, we need to know the corresponding mass of the solution. Using the solution density given, we can convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



For proper unit cancellation, the 0.500-L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/g solution:

$$500\ \text{mL solution}\ \left(\frac{1.19\ \text{g solution}}{\text{mL solution}}\right)\left(\frac{37.2\ \text{g HCl}}{100\ \text{g solution}}\right) = 221\ \text{g HCl}$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

Exercise 14.4b

What volume of concentrated HCl solution contains 125 g of HCl?

Check Your Answer

2

Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a **volume percentage**, %vol or (v/v)%:

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

Example 14.3c

Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$(335\text{ mL solution})(\frac{70\text{ isoproryl alcohol}}{100\text{ mL solution}})(\frac{0.785\text{ g isoproryl alcohol}}{1\text{ mL isopropyl alcohol}}) = 195\text{ g isopropyl alcohol}$$

Exercise 14.4c

Wine is approximately 12% ethanol (CH_3CH_2OH) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

Check Your Answer[3]

Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A **mass-volume percent** is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per decilitre (100 mL) of blood (Figure 14.4b).

(a) (b)

Figure 14.4b “Mixed” mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: work by Samuel Ramos, Unsplash license; credit b: modification of work by Biswarup Ganguly, CC BY 3.0)

Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as **parts per million (ppm)** or **parts per billion (ppb)**. Like percentage (“part per hundred”) units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm}$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppm}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure 14.4c).

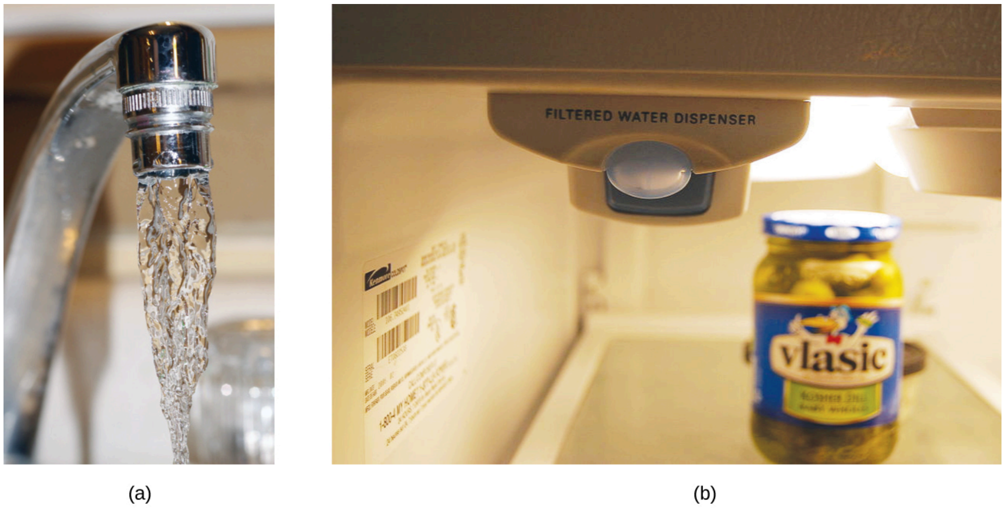

(a) (b)

Figure 14.4c (a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey, CC BY 2.0; credit b: modification of work by vastateparkstaff, CC BY 2.0)

Example 14.4d

Calculation of Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

$$15 \text{ ppb} \times \frac{1 \text{ ppm}}{10^3 \text{ ppb}} = 0.015 \text{ ppm}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \text{ ppb}}$$

$$\text{mass solute} = \frac{15 \text{ ppb} \times 300 \text{ mL} \times \frac{1.00 \text{ g}}{\text{mL}}}{10^9 \text{ ppb}} = 4.5 \times 10^{-6} \text{ g}$$

Finally, convert this mass to the requested unit of micrograms:

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \mu\text{g}}{10^{-6} \text{ g}} = 4.5 \mu\text{g}$$

Exercise 14.4d

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Check Your Answer[4]

Key Equations

- $\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$
- $\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \text{ ppm}$
- $\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \text{ ppb}$

Attribution & References

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Notes

1. 14.8%
2. 282 mL
3. 1.5 mol ethanol
4. 9.6 ppm, 9600 ppb

14.5 COLLIGATIVE PROPERTIES AND OSMOSIS

Learning Objectives

By the end of this section, you will be able to:

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapour pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is denser, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These **colligative properties** include vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

$$M=\frac{\text{mol solute}}{\text{L solution}}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, X, of a component is the ratio of its molar amount to the total number of moles of all solution components:

$$X_{\text{A}}=\frac{\text{mol A}}{\text{total mol of all components}}$$

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$$m=\frac{\text{mol solute}}{\text{kg solvent}}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

Example 14.5a

Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $C_2H_4(OH)_2$, in a solution prepared from 2.22×10^3 g of ethylene glycol and 2.00×10^3 g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the unit definition.

$$\text{mol } \mathrm{C_2H_4(OH)_2}=2220\text{ g}\ \times\ \frac{1\text{ mol }\mathrm{C_2H_4(OH)_2}}{62.07\text{ g }\mathrm{C_2H_4(OH)_2}}=35.8\text{ mol }\mathrm{C_2H_4(OH)_2}$$

$$\text{mol H}_2\text{O} = 2000\text{ g } \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}} = 11.1\text{ mol H}_2\text{O}$$

$$X_{\text{ethylene glycol}} = \frac{35.8\text{ mol C}_2\text{H}_4(\text{OH})_2}{(35.8\ +\ 11.1)\text{ mol total}} = 0.763$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) To find molality, we need to know the moles of the solute and the mass of the solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

$$2220\text{ g C}_2\text{H}_4(\text{OH})_2\ (\frac{\text{mol C}_2\text{H}_2(\text{OH})_2}{62.07\text{ g}}) = 35.8\text{ mol C}_2\text{H}_4(\text{OH})_2$$

Then, convert the mass of the water from grams to kilograms:

$$2000\text{ g H}_2\text{O}\ (\frac{1\text{ kg}}{1000\text{ g}}) = 2\text{ kg H}_2\text{O}$$

Finally, calculate molarity per its definition:

$$\begin{aligned}\text{molality} &= \frac{\text{mol solute}}{\text{kg solvent}}\\ \text{molality} &= \frac{35.8\text{ mol C}_2\text{H}_4(\text{OH})_2}{2\text{ kg H}_2\text{O}}\\ \text{molality} &= 17.9\ m\end{aligned}$$

Exercise 14.5a

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3, dissolved in 125 g of water?

Check Your Answer[1]

Example 14.5b

Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

$$\frac{3.0 \text{ mol NaCl}}{1.0 \text{ kg H}_2\text{O}}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

$$1.0 \text{ kg H}_2\text{O} \left(\frac{1000 \text{ g}}{1 \text{ kg}}\right)\left(\frac{\text{mol H}_2\text{O}}{18.02 \text{ g}}\right) = 55 \text{ mol H}_2\text{O}$$

and then substituting these molar amounts into the definition for mole fraction.

$$\begin{aligned}
X_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\
X_{\text{H}_2\text{O}} &= \frac{55 \text{ mol H}_2\text{O}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\
X_{\text{H}_2\text{O}} &= 0.95 \\
X_{\text{NaCl}} &= \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\
X_{\text{NaCl}} &= \frac{3.0 \text{ mol NaCl}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\
X_{\text{NaCl}} &= 0.052
\end{aligned}$$

Exercise 14.5b

The mole fraction of iodine, I_2, dissolved in dichloromethane, CH_2Cl_2, is 0.115. What is the molal concentration, *m*, of iodine in this solution?

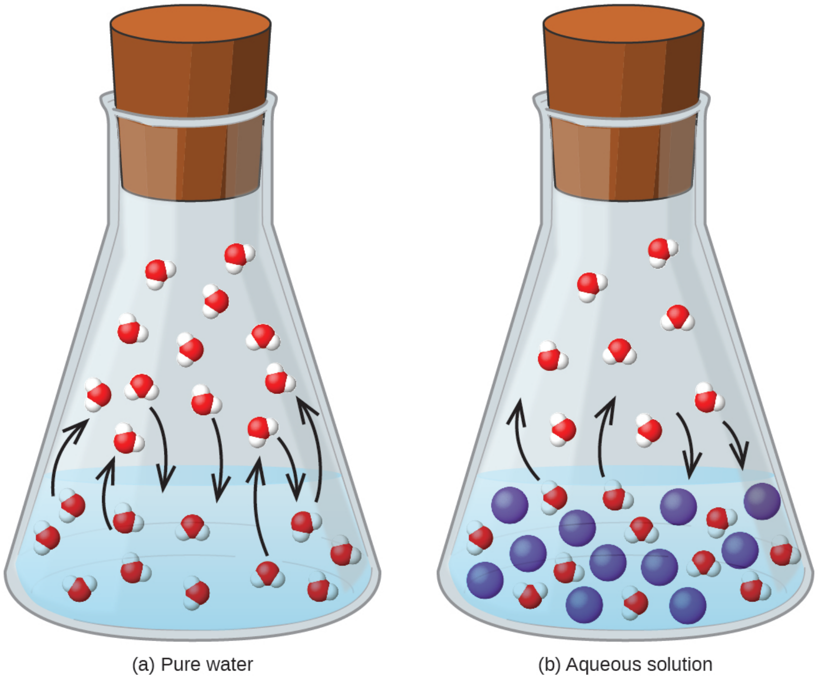
Check Your Answer[2]

Vapour Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapour pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

$$\text{liquid} \leftrightharpoons \text{gas}$$

Dissolving a nonvolatile substance in volatile liquid results in a lowering of the liquid's vapour pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapour phase (i.e., at a lower vapour pressure) (Figure 14.5a). While this kinetic interpretation is useful, it does not account for several important aspects of the colligative nature of vapour pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapour pressure, it is adequate to note that the greater entropy of a solution in comparison to its separate solvent and solute serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapour pressure result and a correspondingly higher boiling point is described in the next section of this module.


(a) Pure water

(b) Aqueous solution

Figure 14.5a The presence of nonvolatile solutes lowers the vapour pressure of a solution by impeding the evaporation of solvent molecules (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The relationship between the vapour pressures of solution components and the concentrations of those components is described by **Raoult's law:** *The partial pressure exerted by any component of an ideal solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.*

$$P_{\mathrm{A}} = X_{\mathrm{A}} P_{\mathrm{A}}^{\circ}$$

where P_{A} is the partial pressure exerted by component A in the solution, P_{A}° is the vapour pressure of pure A, and X_{A} is the mole fraction of A in the solution. (Mole fraction is a concentration unit introduced in the chapter on gases.)

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton's law of partial pressures), the total vapour pressure exerted by a solution containing *i* components is

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^\circ$$

A nonvolatile substance is one whose vapour pressure is negligible ($P^\circ \approx 0$), and so the vapour pressure above a solution containing only nonvolatile solutes is due only to the solvent:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$$

Example 14.5c

Calculation of a Vapour Pressure

Compute the vapour pressure of an ideal solution containing 92.1 g of glycerin, $C_3H_5(OH)_3$, and 184.4 g of ethanol, C_2H_5OH, at 40 °C. The vapour pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapour pressure may be computed per Raoult's law as:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$$

First, calculate the molar amounts of each solution component using the provided mass data.

$$92.1 \cancel{\text{g C}_3\text{H}_5\text{(OH)}_3} \times \frac{1 \text{ mol C}_3\text{H}_5\text{(OH)}_3}{92.094 \cancel{\text{g C}_3\text{H}_5\text{(OH)}_3}} = 1.00 \text{ mol C}_3\text{H}_5\text{(OH)}_3$$

$$184.4 \cancel{\text{g C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.069 \cancel{\text{g C}_2\text{H}_5\text{OH}}} = 4.000 \text{ mol C}_2\text{H}_5\text{OH}$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult's law to compute the solution's vapour pressure.

$$X_{\text{C}_2\text{H}_5\text{OH}} = \frac{4.000 \text{ mol}}{(1.00 \text{ mol} + 4.000 \text{ mol})} = 0.800$$

$$P_{\text{solv}} = X_{\text{solv}} P_{\text{solv}}^\circ = 0.800 \times 0.178 \text{ atm} = 0.142 \text{ atm}$$

Exercise 14.5c

A solution contains 5.00 g of urea, $CO(NH_2)_2$ (a nonvolatile solute) and 0.100 kg of water. If the vapour pressure of pure water at 25 °C is 23.7 torr, what is the vapour pressure of the solution?

Check Your Answer[3]

Elevation of the Boiling Point of a Solvent

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapour pressure is equal to ambient atmospheric pressure. Since the vapour pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Compared to pure solvent, a solution, therefore, will require a higher temperature to achieve any given vapour pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_{b}, is called **boiling point elevation** and is directly proportional to the molal concentration of solute species:

$$\Delta T_{\mathrm{b}} = K_{\mathrm{b}} m$$

where K_{b} is the **boiling point elevation constant**, or the *ebullioscopic constant,* and m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_{b} for several solvents are listed in Table 14.5a.

Table 14.5a Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

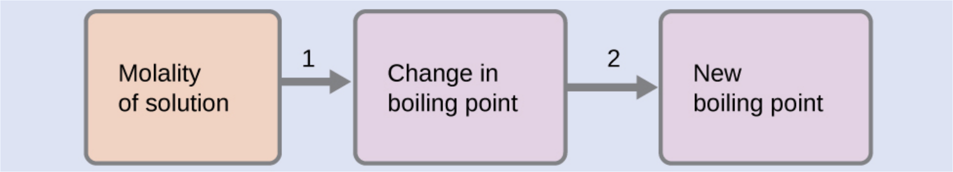
Solvent	**Boiling Point (°C at 1 atm)**	K_{b} **(Cm^{-1})**	**Freezing Point (°C at 1 atm)**	K_{f} **(Cm^{-1})**
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

The extent to which the vapour pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

Example 14.5d

Calculating the Boiling Point of a Solution

What is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?



Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.

1. *Calculate the change in boiling point.*

$$\Delta T_{\mathrm{b}} = K_{\mathrm{b}}m = 2.53\ ^{\circ}\mathrm{C}m^{-1}\ \times\ 0.33\ m = 0.83\ ^{\circ}\mathrm{C}$$

2. *Add the boiling point elevation to the pure solvent's boiling point.*

$$\text{Boiling temperature} = 80.1\ ^{\circ}\mathrm{C}\ +\ 0.83\ ^{\circ}\mathrm{C} = 80.9\ ^{\circ}\mathrm{C}$$

Exercise 14.5d

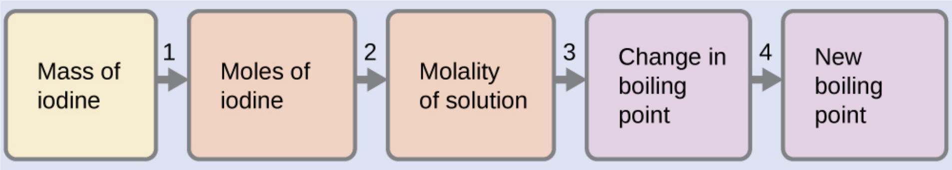
What is the boiling point of the antifreeze with a molality of 17.9 *m* in Example 14.5a (Hint: Water is the solvent).

Check Your Answer[4]

Example 14.5e

The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2, in 800.0 g of chloroform, $CHCl_3$, assuming that the iodine is nonvolatile and that the solution is ideal.



Solution

We can solve this problem using four steps.

1. *Convert from grams to moles of* I_2 *using the molar mass of* I_2 *in the unit conversion factor.*
   Result: 0.363 mol
2. *Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.*
   Result: 0.454 *m*
3. *Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.*
   Result: 1.65 °C
4. *Determine the new boiling point from the boiling point of the pure solvent and the change.*
   Result: 62.91 °C
   Check each result as a self-assessment.

Exercise 14.5e

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

Check Your Answer[5]

Distillation of Solutions

Distillation is a technique for separating the components of mixtures that is widely applied both in the laboratory and in industrial settings. It is used to refine petroleum, to isolate fermentation products, and to purify water. This separation technique involves the controlled heating of a sample mixture to selectively vaporize, condense, and collect one or more components of interest. A typical apparatus for laboratory-scale distillations is shown in Figure 14.5d.

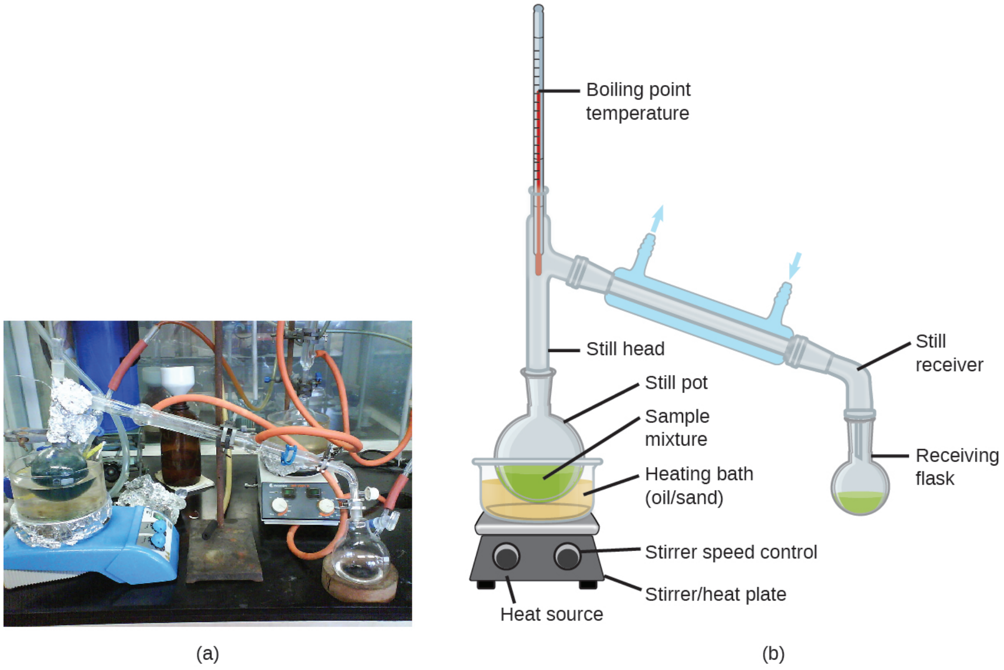


Figure 14.5b A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by Rifleman82, PD; credit b: modification of work adapted by Slashme, PD in *Chemistry (OpenStax)*, CC BY 4.0).

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in Figure 14.5c.

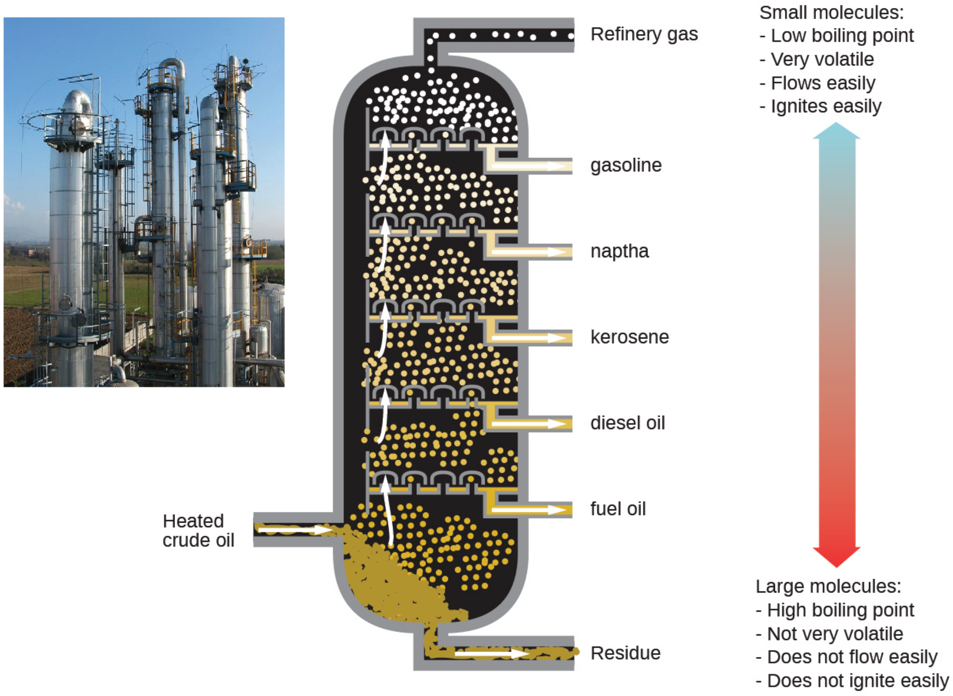


Figure 14.5c Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures. (credit: modification of work by Luigi Chiesa, CC BY 3.0 in *Chemistry (OpenStax)*, CC BY 4.0).)

Depression of the Freezing Point of a Solvent

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt (Figure 14.5d), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than freshwater, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).

Figure 14.5d Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker, CC BY 2.0)

The decrease in the freezing point of a dilute solution compared to that of the pure solvent, ΔT_f, is called the **freezing point depression** and is directly proportional to the molal concentration of the solute

$$\Delta T_\text{f} = K_\text{f} m$$

where m is the molal concentration of the solute in the solvent and K_f is called the **freezing point depression constant** (or *cryoscopic constant*). Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in Table 14.5a.

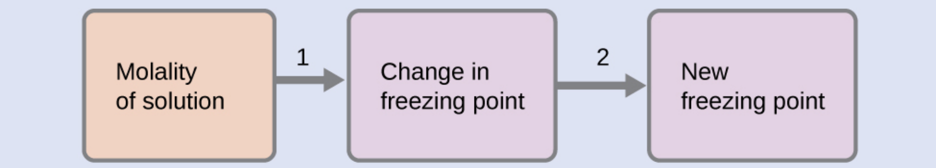
Example 14.5f

Calculation of the Freezing Point of a Solution

What is the freezing point of the 0.33 m solution of a nonvolatile nonelectrolyte solute in benzene described in Example 14.5b?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



1. *Calculate the change in freezing point.*

$$\Delta T_{\text{f}} = K_{\text{f}}m = 5.12\ {}^{\circ}\text{C}m^{-1}\ \times\ 0.33m = 1.7\ {}^{\circ}\text{C}$$

2. *Subtract the freezing point change observed from the pure solvent's freezing point.*

$$\textbf{Freezing temperature} = 5.5\ {}^{\circ}\text{C}\ -\ 1.7\ {}^{\circ}\text{C} = 3.8\ {}^{\circ}\text{C}$$

Exercise 14.5f

What is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Check Your Answer[6]

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride ("rock salt") for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Figure 14.5e).

Figure 14.5e Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft. (credit a: work by Oregon Department of Transportation, CC BY 2.0; credit b: work by Paolo Cerutti, CC BY 2.0)

Phase Diagram for an Aqueous Solution of a Nonelectrolyte

The colligative effects on vapour pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid. Phase diagrams for water and an aqueous solution are shown in Figure 14.5f.

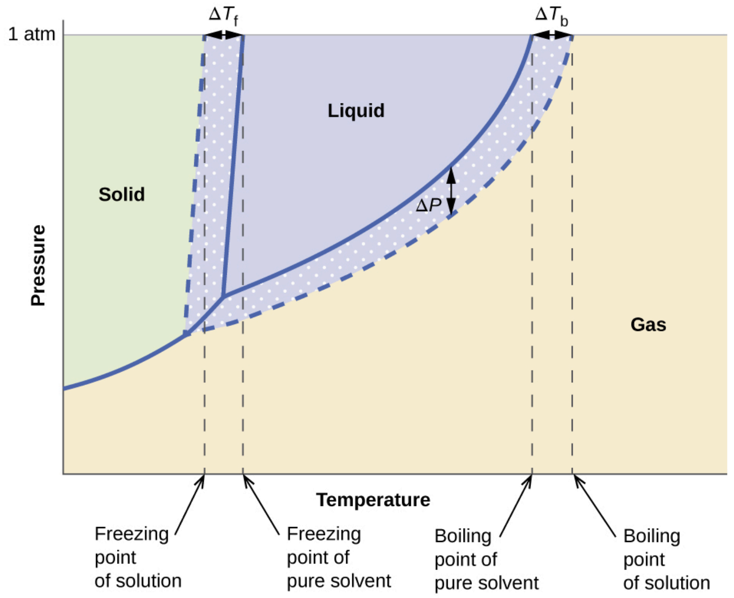


Figure 14.5f These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The liquid-vapour curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapour pressure *lowering*, ΔP, that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b, associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔT_b, that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed solvent only, and so transitions between these phases are not subject to colligative effects.

Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as **semipermeable membranes.**

Consider the apparatus illustrated in Figure 14.5g, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than in the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as **osmosis.**

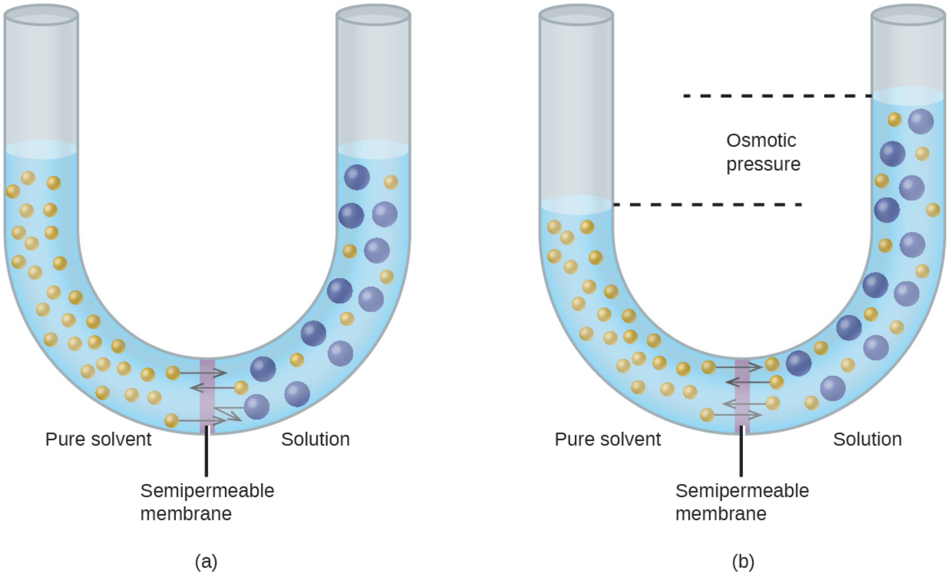


Figure 14.5g Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration in *Chemistry (OpenStax)*, CC BY 4.0).

When osmosis is carried out in an apparatus like that shown in Figure 14.5g, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the **osmotic pressure (Π)** of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M, and absolute temperature, T, according to the equation

$$\Pi = MRT$$

where R is the universal gas constant.

Example 14.5g

Calculation of Osmotic Pressure

What is the osmotic pressure (atm) of a 0.30 *M* solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

We can find the osmotic pressure, Π, using the formula $\Pi = MRT$, where T is on the Kelvin scale (310 K) and the value of R is expressed in appropriate units (0.08206 L atm/mol K).

$$\begin{aligned} \Pi &= MRT \\ &= \mathbf{0.03\ mol/L\ \times\ 0.08206\ L\ atm/mol\ K\ \times\ 310\ K} \\ &= \mathbf{7.6\ atm} \end{aligned}$$

Exercise 14.5g

What is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH, in water at 37 °C

Check Your Answer[7]

If a solution is placed in an apparatus like the one shown in Figure 14.5h, applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.

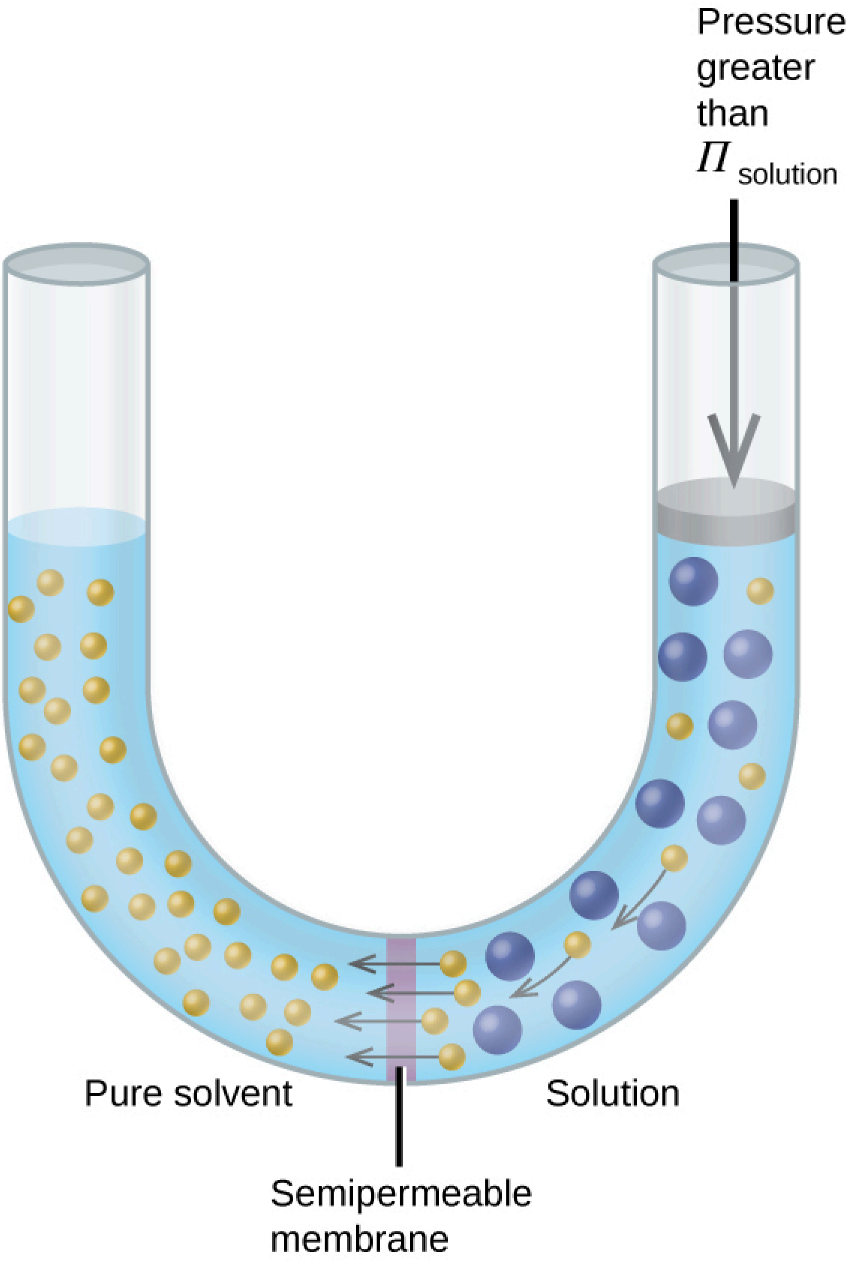


Figure 14.5h Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent in *Chemistry (OpenStax)*, CC BY 4.0).

Reverse Osmosis Water Purification

In the process of osmosis, diffusion serves to move water through a semipermeable membrane from a less concentrated solution to a more concentrated solution. Osmotic pressure is the amount of pressure that must be applied to the more concentrated solution to cause osmosis to stop. If greater pressure is applied, the water will go from the more concentrated solution to a less concentrated (more pure) solution. This is called reverse osmosis. Reverse osmosis (RO) is used to purify water in many applications, from desalination plants in coastal cities, to water-purifying machines in grocery stores, and smaller reverse-osmosis household units. With a hand-operated pump, small RO units can be used in third-world countries, disaster areas, and in lifeboats. Our military forces have a variety of generator-operated RO units that can be transported in vehicles to remote locations.

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be **isotonic** with blood serum. If a less concentrated solution, a **hypotonic** solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called **hemolysis**. When a more concentrated solution, a **hypertonic** solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called **crenation**. These effects are illustrated in Figure 14.5i.

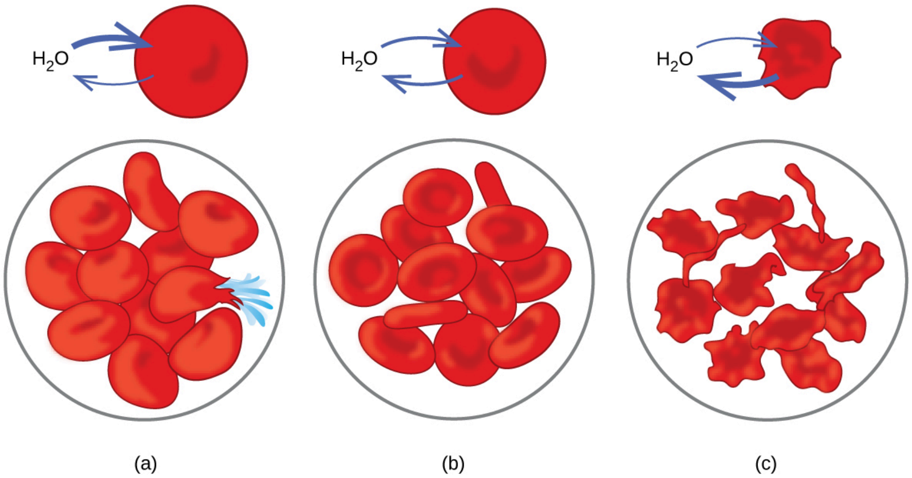


Figure 14.5i Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by LadyofHats, PD in *Chemistry (OpenStax)*, CC BY 4.0).

Determination of Molar Masses

Osmotic pressure and changes in freezing point, boiling point, and vapour pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

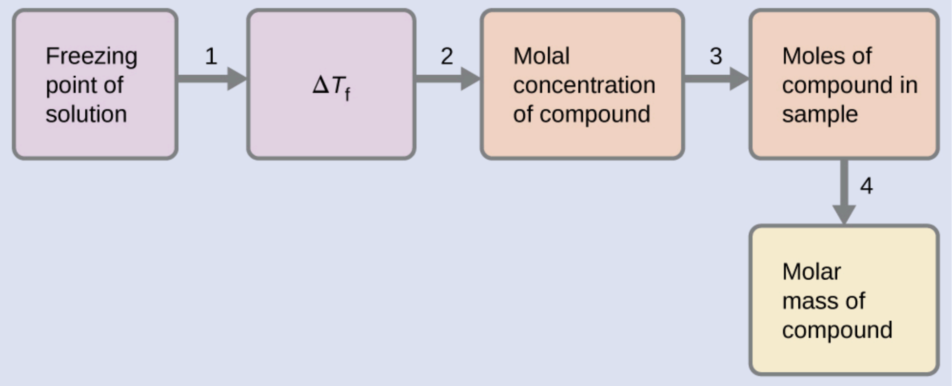
Example 14.5h

Determination of a Molar Mass from a Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



1. Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene (Table 14.5a).
$$\Delta T_\text{f} = 5.5\ ^\circ\text{C}\ -\ 2.32\ ^\circ\text{C} = 3.2\ ^\circ\text{C}$$
2. Determine the molal concentration from K_f, the freezing point depression constant for benzene (Table 14.5a), and ΔT_f.
$$\Delta T_\text{f} = K_\text{f} m$$
$$m = \frac{\Delta T_\text{f}}{K_\text{f}} = \frac{3.2\ ^\circ\text{C}}{5.12\ ^\circ\text{C}m^{-1}} = 0.63m$$
3. Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.

$$\text{Moles of solute} = \frac{0.62\ \text{mol solute}}{1.00\ \cancel{\text{kg solvent}}} \times 0.0550\ \cancel{\text{kg solvent}} = 0.035\ \text{mol}$$

4. Determine the molar mass from the mass of the solute and the number of moles in that mass.

$$\text{Molar mass} = \frac{4.00\ \text{g}}{0.034\ \text{mol}} = 1.2 \times 10^2\ \text{g/mol}$$

Exercise 14.5h

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. What is the molar mass of this compound?

Check Your Answer[8]

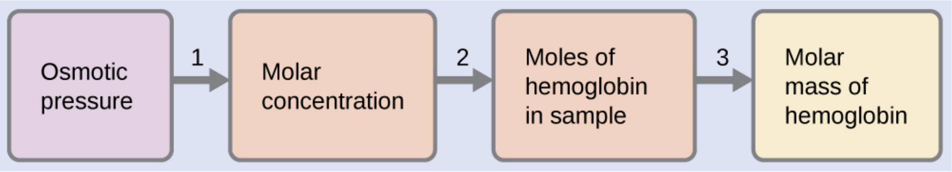
Example 14.5i

Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1. *Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.*

$$\Pi = \frac{5.9 \text{ torr } \times \text{ } 1 \text{ atm}}{760 \text{ torr}} = 7.8 \times 10^{-3} \text{ atm}$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L atm/mol K})(295 \text{ K})} = 3.2 \times 10^{-4} \text{ M}$$

2. *Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.*

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4} \text{ mol}}{1 \cancel{\text{ L solution}}} \times 0.500 \cancel{\text{ L solution}} = 1.6 \times 10^{-4} \text{ mol}$$

3. *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^{4} \text{ g/mol}$$

Exercise 14.5i

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of the solution has an osmotic pressure of 0.56 torr at 25 °C?

Check Your Answer[9]

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the kind, of solute species dissolved. For example, 1 mole of any nonelectrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms *2 moles* of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

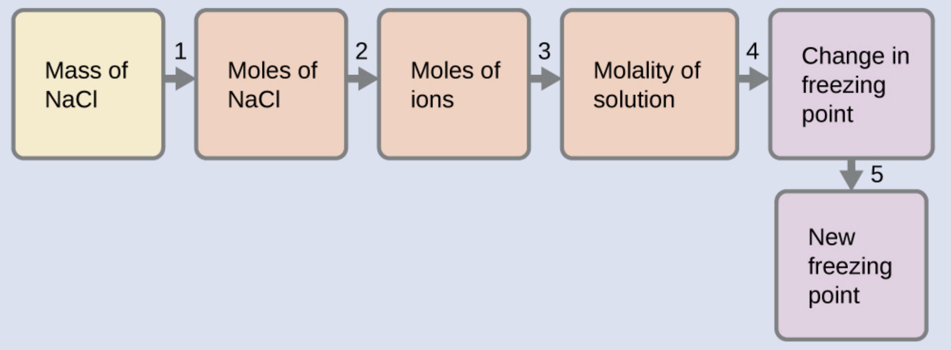
Example 14.5j

The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of water as a nonelectrolyte molecule, and determine the freezing temperature the solution (which is approximately equal to the freezing temperature of seawater).

Solution

We can solve this problem using the following series of steps.



1. *Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor.*
   Result: 0.072 mol NaCl
2. *Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl).*
   Result: 0.14 mol ions
3. *Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms.*
   Result: 1.1 m
4. *Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes.*
   Result: 2.0 °C
5. *Determine the new freezing point from the freezing point of the pure solvent and the change.*
   Result: −2.0 °C
   Check each result as a self-assessment.

Exercise 14.5j

Assume that each of the ions in calcium chloride, $CaCl_2$, has the same effect on the freezing point of water as a nonelectrolyte molecule. Calculate the freezing point of a solution of 0.724 g of $CaCl_2$ in 175 g of water.

Check Your Answer[10]

Assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 1.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

$$\Delta T_{\text{f}} = 2.0\ \text{mol ions/kg water}\ \times\ 1.86\ {}^{\circ}\text{C kg water/mol ion} = 3.7\ {}^{\circ}\text{C}.$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honour of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The **van't Hoff factor (*i*)** is defined as the ratio of solute particles in solution to the number of formula units dissolved:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in Table 14.5b.

Table 14.5b Expected and Observed van't Hoff Factors for Several 0.050 *m* Aqueous Electrolyte Solutions

Electrolyte	Particles in Solution	*i* (Predicted)	*i* (Measured)
HCl	H^+, Cl^-	2	1.9
NaCl	Na^+, Cl^-	2	1.9
$MgSO_4$	Mg^{2+}, SO_4^{2-}	2	1.3
$MgCl_2$	Mg^{2+}, $2Cl^-$	3	2.7
$FeCl_3$	Fe^{3+}, $3Cl^-$	4	3.4
glucose[11]	$C_{12}H_{22}O_{11}$	1	1.0

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (Figure 14.5j). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table 14.5b are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

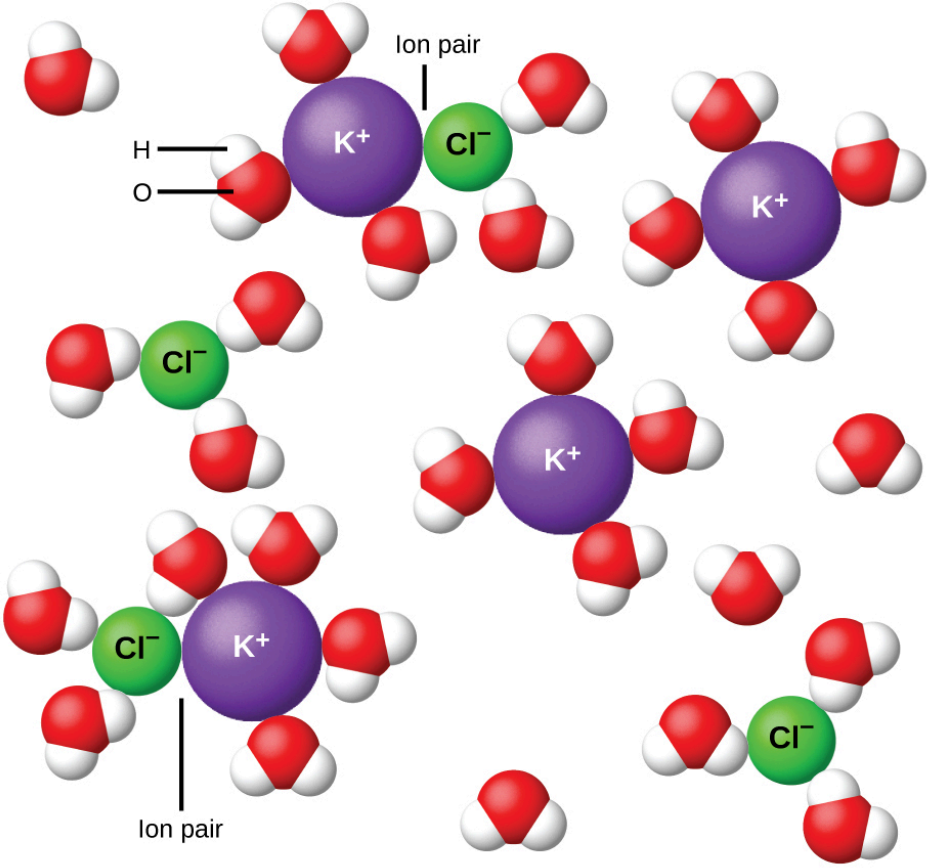


Figure 14.5j Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Key Equations

- $(P_A = X_A P_A^\circ)$
- $P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^\circ$
- $P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$
- $\Delta T_b = K_b m$
- $\Delta T_f = K_f m$
- $\Pi = MRT$

Attribution & References

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Notes

1. 7.14×10^{-3}; 0.399 *m*
2. 1.50 *m*
3. 23.4 torr
4. 109.2 °C
5. 100.12 °C
6. −9.3 °C
7. 5.3 atm
8. 1.8×10^{2} g/mol
9. 2.7×10^{4} g/mol
10. −0.208 °C
11. A nonelectrolyte shown for comparison.

14.6 COLLOIDS

Learning Objectives

By the end of this section, you will be able to:

- Describe the composition and properties of colloidal dispersions
- List and explain several technological applications of colloids

As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These suspensions are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing. On the other hand, when we make a solution, we prepare a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behaviour from suspensions. A solution may be coloured, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing. A group of mixtures called **colloids** (or colloidal dispersions) exhibit properties intermediate between those of suspensions and solutions (Figure 14.6a). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.

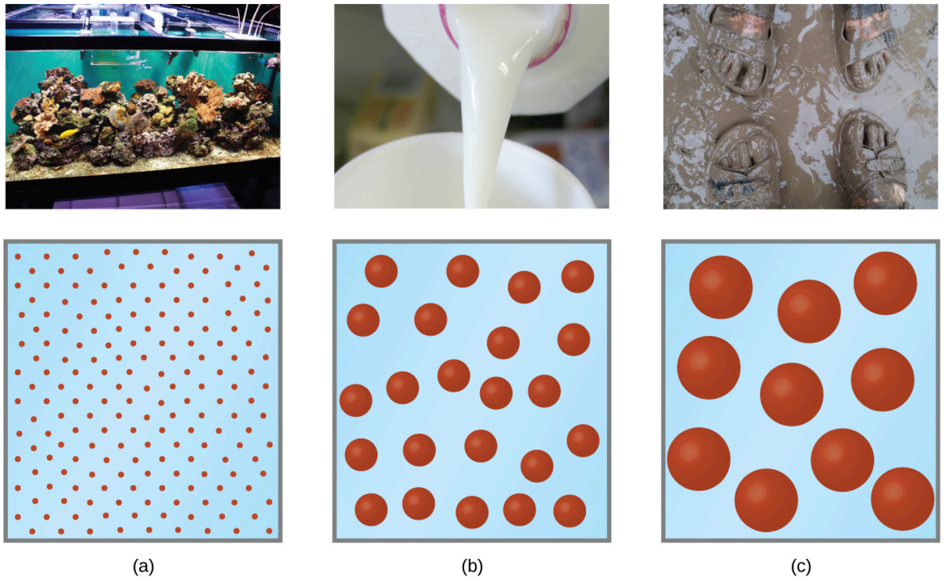

Figure 14.6a (a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are much larger but remain dispersed and do not settle. (c) A suspension, such as mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt, CC BY 2.0; credit b photo: modification of work by Melissa Wiese, CC BY 2.0; credit c photo: modification of work by Peter Burgess, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).

The particles in a colloid are large enough to scatter light, a phenomenon called the **Tyndall effect.** This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in Figure 14.6b. Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.

Figure 14.6b The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: work by Bahman, CC BY 2.0)

The term “colloid”—from the Greek words *kolla*, meaning “glue,” and *eidos*, meaning “like”—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as “solute” and “solvent,” the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the **dispersed phase** and the substance or solution throughout which the particulate is dispersed is called the **dispersion medium**. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in Table 14.6a.

Table 14.6a Examples of Colloidal Systems

Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some coloured gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion
liquid	solid	jellies, gels, pearl, opal (H_2O in SiO_2)	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam
gas	solid	pumice, floating soaps	—

Preparation of Colloidal Systems

We can prepare a colloidal system by producing particles of colloidal dimensions and distributing these particles throughout a dispersion medium. Particles of colloidal size are formed by two methods:

1. Dispersion methods: that is, by breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
2. Condensation methods: that is, growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Powdered milk particles of colloidal size are produced by dehydrating milk spray. Some atomizers produce colloidal dispersions of a liquid in air.

We can prepare an **emulsion** by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an **emulsifying agent,** a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents.

Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions. We can prepare a red colloidal suspension of iron(III) hydroxide by mixing a concentrated solution of iron(III) chloride with hot water:

$\mathrm{Fe^{3+}}(aq)\ +\ \mathrm{3Cl^{-}}(aq)\ +\ \mathrm{6H_2O}(l) \longrightarrow \mathrm{Fe(OH)_3}(s)\ +\ \mathrm{H_3O^{+}}(aq)\ +\ \mathrm{3Cl^{-}}(aq).$

A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

$$\mathrm{Au^{3+}}\ +\ \mathrm{3e^{-}} \longrightarrow \mathrm{Au}$$

Some gold sols prepared in 1857 are still intact (the particles have not coalesced and settled), illustrating the long-term stability of many colloids.

Soaps and Detergents

Pioneers made soap by boiling fats with a strongly basic solution made by leaching potassium carbonate, K_2CO_3, from wood ashes with hot water. Animal fats contain polyesters of fatty acids (long-chain carboxylic acids). When animal fats are treated with a base like potassium carbonate or sodium hydroxide, glycerol and salts of fatty acids such as palmitic, oleic, and stearic acid are formed. The salts of fatty acids are called *soaps*. The sodium salt of stearic acid, sodium stearate, has the formula $C_{17}H_{35}CO_2Na$ and contains an uncharged nonpolar hydrocarbon chain, the $C_{17}H_{35}$— unit, and an ionic carboxylate group, the $—\mathrm{CO_2}^{-}$ unit (Figure 14.6c).

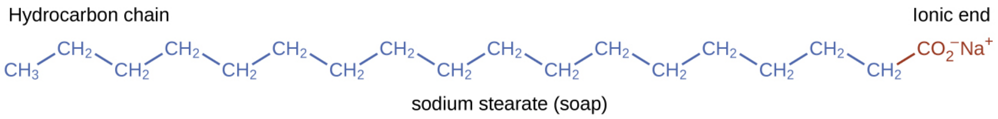

Figure 14.6c Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). An ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Detergents (soap substitutes) also contain nonpolar hydrocarbon chains, such as $C_{12}H_{25}$—, and an ionic group, such as a sulfate—$OSO_3{}^-$, or a sulfonate—$SO_3{}^-$ (Figure 14.6d). Soaps form insoluble calcium and magnesium compounds in hard water; detergents form water-soluble products—a definite advantage for detergents.

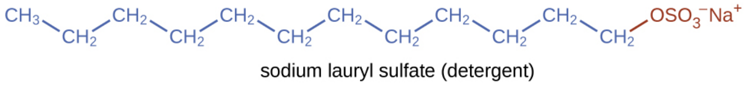

Figure 14.6d Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The cleaning action of soaps and detergents can be explained in terms of the structures of the molecules involved. The hydrocarbon (nonpolar) end of a soap or detergent molecule dissolves in, or is attracted to, nonpolar substances such as oil, grease, or dirt particles. The ionic end is attracted by water (polar), illustrated in Figure 14.6e. As a result, the soap or detergent molecules become oriented at the interface between the dirt particles and the water so they act as a kind of bridge between two different kinds of matter, nonpolar and polar. Molecules such as this are termed **amphiphilic** since they have both a hydrophobic (“water-fearing”) part and a hydrophilic (“water-loving”) part. As a consequence, dirt particles become suspended as colloidal particles and are readily washed away.

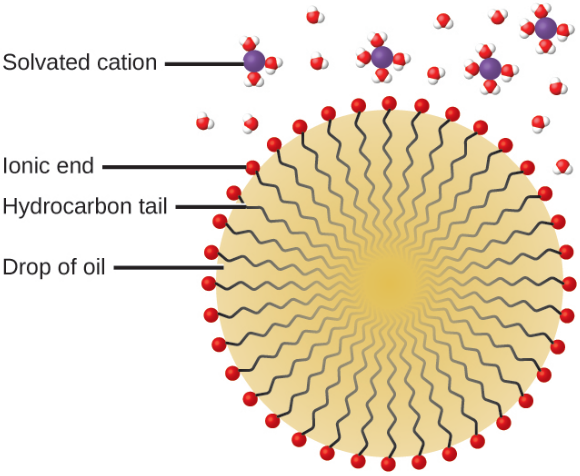

Figure 14.6e This diagrammatic cross-section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Deepwater Horizon Oil Spill

The blowout of the Deepwater Horizon oil drilling rig on April 20, 2010, in the Gulf of Mexico near Mississippi, began the largest marine oil spill in the history of petroleum. In the 87 days following the blowout, an estimated 4.9 million barrels (210 million gallons) of oil flowed from the ruptured well 5000 feet below the water's surface. The well was finally declared sealed on September 19, 2010.

Crude oil is immiscible with and less dense than water, so the spilled oil rose to the surface of the water. Floating booms, skimmer ships, and controlled burns were used to remove oil from the water's surface in an attempt to protect beaches and wetlands along the Gulf coast. In addition to the removal of the oil, attempts were also made to lessen its environmental impact by rendering it "soluble" (in the loose sense of the term) and thus allowing it to be diluted to hopefully less harmful levels by the vast volume of ocean water. This approach used 1.84 million gallons of the oil dispersant Corexit 9527, most of which was injected underwater at the site of the leak, with small amounts being sprayed on top of the spill. Corexit 9527 contains 2-butoxyethanol ($C_6H_{14}O_2$), an amphiphilic molecule whose polar and nonpolar ends are useful for emulsifying oil into small droplets, increasing the surface area of the oil and making it more available to marine bacteria for digestion. While this approach avoids many of the immediate hazards that bulk oil poses to marine and coastal ecosystems, it introduces the possibility of long-term effects resulting from the introduction of the complex and potentially toxic components of petroleum into the ocean's food chain. A number of organizations are involved in monitoring the extended impact of this oil spill, including the National Oceanic and Atmospheric Administration (Gulf Spill Restoration).

Electrical Properties of Colloidal Particles

Dispersed colloidal particles are often electrically charged. A colloidal particle of iron(III) hydroxide, for example, does not contain enough hydroxide ions to compensate exactly for the positive charges on the iron(III) ions. Thus, each individual colloidal particle bears a positive charge, and the colloidal dispersion consists of charged colloidal particles and some free hydroxide ions, which keep the dispersion electrically neutral. Most metal hydroxide colloids have positive charges, whereas most metals and metal sulfides form negatively charged dispersions. All colloidal particles in any one system have charges of the same sign. This helps keep them dispersed because particles containing like charges repel each other.

We can take advantage of the charge on colloidal particles to remove them from a variety of mixtures. If we place a colloidal dispersion in a container with charged electrodes, positively charged particles, such as iron(III) hydroxide particles, would move to the negative electrode. There, the colloidal particles lose their charge and coagulate as a precipitate.

The carbon and dust particles in smoke are often colloidally dispersed and electrically charged. Frederick Cottrell, an American chemist, developed a process to remove these particles (Figure 14.6f).

Frederick Gardner Cottrell

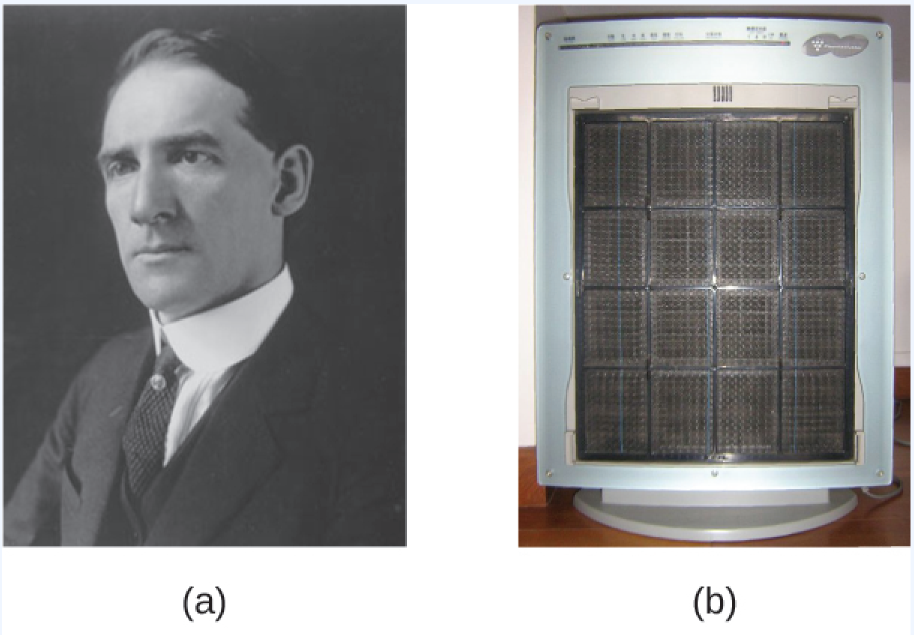

Figure 14.6f (a) Frederick Cottrell developed (b) the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. (credit a: work by unknown, PD; credit b: modification of work by SpLot, CC BY-SA 3.0)

Born in Oakland, CA in 1877, Frederick Cottrell devoured textbooks as if they were novels and graduated from high school at the age of 16. He then entered the University of California (UC), Berkeley, completing a Bachelor's degree in three years. He saved money from his $1200 annual salary as a chemistry teacher at Oakland High School to fund his studies in chemistry in Berlin with Nobel prize winner Jacobus Henricus van't Hoff, and in Leipzig with Wilhelm Ostwald, another Nobel awardee. After earning his PhD in physical chemistry, he returned to the United States to teach at UC Berkeley. He also consulted for the DuPont Company, where he developed the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. Cottrell used the proceeds from his invention to fund a nonprofit research corporation to finance scientific research.

The charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust (Figure 14.6g). This is one of the important methods used to clean up the smoke from a variety of industrial processes. The process is also important in the recovery of valuable products from the smoke and flue dust of smelters, furnaces, and kilns. There are also ionic air filters designed for home use to improve indoor air quality.

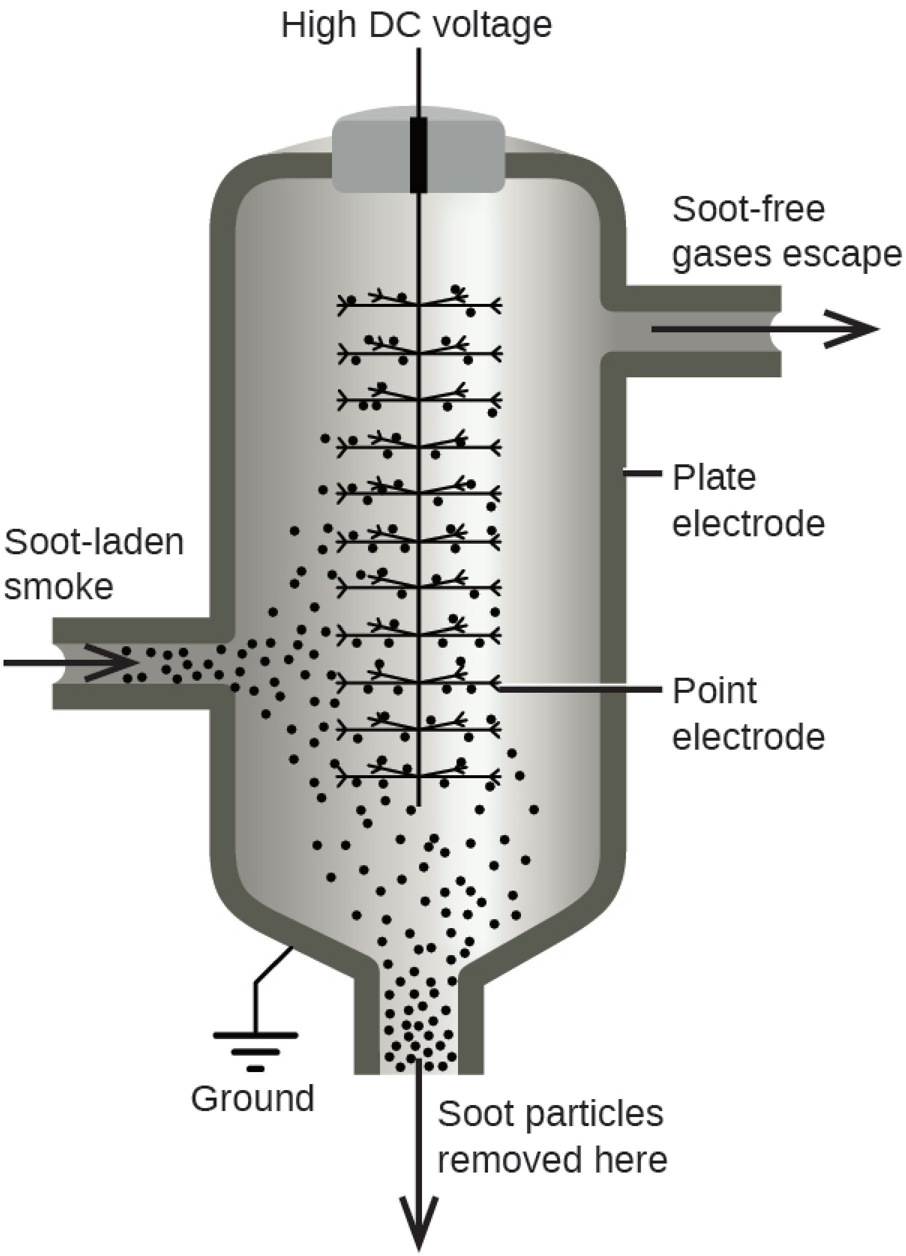

Figure 14.6g In a Cottrell precipitator, positively and negatively charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust.

Gels

When we make gelatin, such as Jell-O, we are making a type of colloid (Figure 14.6h). Gelatin sets on cooling because the hot aqueous mixture of gelatin coagulates as it cools and the whole mass, including the liquid, sets to an extremely viscous body known as a **gel**, a colloid in which the dispersing medium is a solid and the dispersed phase is a liquid. It appears that the fibres of the dispersing medium form a complex three-dimensional network, the interstices being filled with the liquid medium or a dilute solution of the dispersing medium. Because the formation of a gel is accompanied by the taking up of water or some other solvent, the gel is said to be hydrated or solvated.

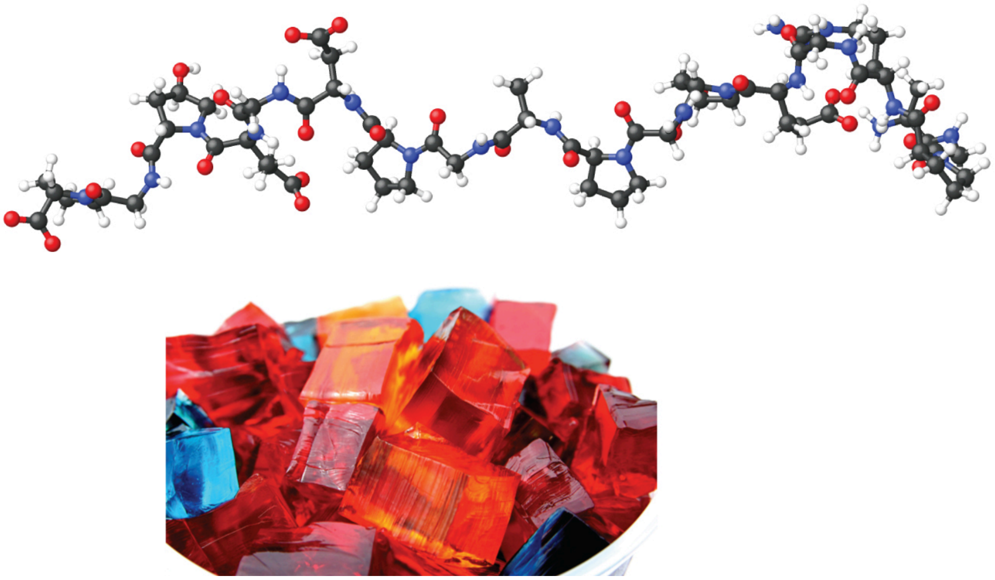

Figure 14.6h Gelatin desserts are colloids in which an aqueous solution of sweeteners and flavours is dispersed throughout a medium of solid proteins. (credit photo: modification of work by Steven Depolo, CC BY 2.0; in *Chemistry (OpenStax)*, CC BY 4.0).)

Pectin, a carbohydrate from fruit juices, is a gel-forming substance important in jelly making. Silica gel, a colloidal dispersion of hydrated silicon dioxide, is formed when dilute hydrochloric acid is added to a dilute solution of sodium silicate. Canned Heat is a gel made by mixing alcohol and a saturated aqueous solution of calcium acetate.

Attribution & References

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CHAPTER 14 - SUMMARY

14.1 – Solutions: An introduction

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

14.2 – Solubility

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

14.3 – Molarity

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per litre of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

14.4 – Other Units for Solution Concentrations

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

14.5 – Colligative Properties and Osmosis

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapour pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

14.6 – Colloids

Colloids are mixtures in which one or more substances are dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium. The particles of a colloid remain dispersed and do not settle due to gravity, and they are often electrically charged. Colloids are widespread in nature and are involved in many technological applications.

Attribution & References

Except where otherwise noted, this page is adapted by Gregory A. Anderson from "11.1 The Dissolution Process", "11.3 Solubility", "6.3 Molarity", "6.4 Other Units for Solution Concentrations", "11.4 Colligative Properties" and "11.5 Colloids" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* . / Extracted and reused key-takeaways and summaries from end of pages.

CHAPTER 14 - REVIEW

14.1 – Solutions: An introduction

1. How do solutions differ from compounds? From other mixtures?
   Check Answer: [1]
2. Which of the principal characteristics of solutions can we see in the solutions of $K_2Cr_2O_7$ shown in Figure 14.1a?
3. When KNO_3 is dissolved in water, the resulting solution is significantly colder than the water was originally.
   a. Is the dissolution of KNO_3 an endothermic or an exothermic process?
   b. What conclusions can you draw about the intermolecular attractions involved in the process?
   c. Is the resulting solution an ideal solution?
   Check Answer: [2]
4. Give an example of each of the following types of solutions:
   a. a gas in a liquid
   b. a gas in a gas
   c. a solid in a solid
5. Indicate the most important types of intermolecular attractions in each of the following solutions:
   a. The solution in Figure 14.1a.
   b. $NO(l)$ in $CO(l)$
   c. $Cl_2(g)$ in $Br_2(l)$
   d. $HCl(aq)$ in benzene $C_6H_6(l)$
   e. Methanol $CH_3OH(l)$ in $H_2O(l)$
   Check Answer: [3]
6. Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane (C_7H_{16}, nonpolar solvent):
   a. vegetable oil (nonpolar)
   b. isopropyl alcohol (polar)
   c. potassium bromide (ionic)
7. Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes. **Check Answer:** [4]
8. Solutions of hydrogen in palladium may be formed by exposing Pd metal to H_2 gas. The concentration

of hydrogen in the palladium depends on the pressure of H_2 gas applied, but in a more complex fashion than can be described by Henry's law. Under certain conditions, 0.94 g of hydrogen gas is dissolved in 215 g of palladium metal.

  a. Determine the molarity of this solution (solution density = 1.8 g/cm^3).
  b. Determine the molality of this solution (solution density = 1.8 g/cm^3).
  c. Determine the percent by mass of hydrogen atoms in this solution (solution density = 1.8 g/cm^3).

14.2 – Solubility

1. Suppose you are presented with a clear solution of sodium thiosulfate, $Na_2S_2O_3$. How could you determine whether the solution is unsaturated, saturated, or supersaturated?
2. Supersaturated solutions of most solids in water are prepared by cooling saturated solutions. Supersaturated solutions of most gases in water are prepared by heating saturated solutions. Explain the reasons for the difference in the two procedures.
   Check Answer: [5]
3. Suggest an explanation for the observations that ethanol, C_2H_5OH, is completely miscible with water and that ethanethiol, C_2H_5SH, is soluble only to the extent of 1.5 g per 100 mL of water.
4. Calculate the percent by mass of KBr in a saturated solution of KBr in water at 10 °C. See Figure 14.2h for useful data, and report the computed percentage to one significant digit. **Check Answer:** [6]
5. Which of the following gases is expected to be most soluble in water? Explain your reasoning.
   a. CH_4
   b. CCl_4
   c. $CHCl_3$
6. At 0 °C and 1.00 atm, as much as 0.70 g of O_2 can dissolve in 1 L of water. At 0 °C and 4.00 atm, how many grams of O_2 dissolve in 1 L of water? **Check Answer:** [7]
7. Refer to Figure 14.2c.
   a. How did the concentration of dissolved CO_2 in the beverage change when the bottle was opened?
   b. What caused this change?
   c. Is the beverage unsaturated, saturated, or supersaturated with CO_2?
8. The Henry's law constant for CO_2 is 3.4×10^{-2} M/atm at 25 °C. What pressure of carbon dioxide is needed to maintain a CO_2 concentration of 0.10 M in a can of lemon-lime soda? **Check Answer:** [8]
9. The Henry's law constant for O_2 is 1.3×10^{-3} M/atm at 25 °C. What mass of oxygen would be dissolved in a 40-L aquarium at 25 °C, assuming an atmospheric pressure of 1.00 atm, and that the partial pressure of O_2 is 0.21 atm?
10. How many litres of HCl gas, measured at 30.0 °C and 745 torr, are required to prepare 1.25 L of a 3.20-M solution of hydrochloric acid? **Check Answer:** [9]

14.3 – Molarity

1. Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.
2. What information do we need to calculate the molarity of a sulfuric acid solution?
   Check Answer: [10]
3. What does it mean when we say that a 200-mL sample and a 400-mL sample of a solution of salt have the same molarity? In what ways are the two samples identical? In what ways are these two samples different?
4. Determine the molarity for each of the following solutions:
   a. 0.444 mol of $CoCl_2$ in 0.654 L of solution
   b. 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution
   c. 0.2074 g of calcium hydroxide, $Ca(OH)_2$, in 40.00 mL of solution
   d. 10.5 kg of $Na_2SO_4{\cdot}10H_2O$ in 18.60 L of solution
   e. 7.0×10^{-3} mol of I_2 in 100.0 mL of solution
   f. 1.8×10^{4} mg of HCl in 0.075 L of solution
   Check Answer: [11]
5. Determine the molarity of each of the following solutions:
   a. 1.457 mol KCl in 1.500 L of solution
   b. 0.515 g of H_2SO_4 in 1.00 L of solution
   c. 20.54 g of $Al(NO_3)_3$ in 1575 mL of solution
   d. 2.76 kg of $CuSO_4{\cdot}5H_2O$ in 1.45 L of solution
   e. 0.005653 mol of Br_2 in 10.00 mL of solution
   f. 0.000889 g of glycine, $C_2H_5NO_2$, in 1.05 mL of solution
6. Consider this question: What is the mass of the solute in 0.500 L of 0.30 M glucose, $C_6H_{12}O_6$, used for intravenous injection?
   a. Outline the steps necessary to answer the question.
   b. Answer the question.
   Check Answer: [12]
7. Consider this question: What is the mass of solute in 200.0 L of a 1.556-M solution of KBr?
   a. Outline the steps necessary to answer the question.
   b. Answer the question.
8. Calculate the number of moles and the mass of the solute in each of the following solutions:
   a. 2.00 L of 18.5 M H_2SO_4, concentrated sulfuric acid
   b. 100.0 mL of $3.8 \times 10^{-5} M$ NaCN, the minimum lethal concentration of sodium cyanide in blood serum
   c. 5.50 L of 13.3 M H_2CO, the formaldehyde used to “fix” tissue samples
   d. 325 mL of $1.8 \times 10^{-6} M$ $FeSO_4$, the minimum concentration of iron sulfate detectable by taste in

drinking water

Check Answer: [13]

9. Calculate the number of moles and the mass of the solute in each of the following solutions:
   a. 325 mL of 8.23 × 10^{-5} *M* KI, a source of iodine in the diet
   b. 75.0 mL of 2.2 × 10^{-5} *M* H_2SO_4, a sample of acid rain
   c. 0.2500 L of 0.1135 *M* K_2CrO_4, an analytical reagent used in iron assays
   d. 10.5 L of 3.716 *M* $(NH_4)_2SO_4$, a liquid fertilizer
10. Consider this question: What is the molarity of $KMnO_4$ in a solution of 0.0908 g of $KMnO_4$ in 0.500 L of solution?
    1. Outline the steps necessary to answer the question.
    2. Answer the question.

    Check Answer: [14]
11. Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
12. Calculate the molarity of each of the following solutions:
    a. 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum
    b. 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia
    c. 1.49 kg of isopropyl alcohol, C_3H_7OH, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol
    d. 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20 °C

    Check Answer: [15]
13. Calculate the molarity of each of the following solutions:
    a. 293 g HCl in 666 mL of solution, a concentrated HCl solution
    b. 2.026 g $FeCl_3$ in 0.1250 L of a solution used as an unknown in general chemistry laboratories
    c. 0.001 mg Cd^{2+} in 0.100 L, the maximum permissible concentration of cadmium in drinking water
    d. 0.0079 g $C_7H_5SNO_3$ in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.
14. There is about 1.0 g of calcium, as Ca^{2+}, in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?

    Check Answer: [16]
15. What volume of a 1.00-*M* $Fe(NO_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 *M*?
16. If 0.1718 L of a 0.3556-*M* C_3H_7OH solution is diluted to a concentration of 0.1222 *M*, what is the volume of the resulting solution?

    Check Answer: [17]
17. If 4.12 L of a 0.850 *M*-H_3PO_4 solution is be diluted to a volume of 10.00 L, what is the concentration

of the resulting solution?

18. What volume of a 0.33-*M* $C_{12}H_{22}O_{11}$ solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 *M*?
    Check Answer: [18]
19. What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-*M* solution is allowed to evaporate until the volume is reduced to 0.105 L?
20. What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?
    a. 1.00 L of a 0.250-*M* solution of $Fe(NO_3)_3$ is diluted to a final volume of 2.00 L
    b. 0.5000 L of a 0.1222-*M* solution of C_3H_7OH is diluted to a final volume of 1.250 L
    c. 2.35 L of a 0.350-*M* solution of H_3PO_4 is diluted to a final volume of 4.00 L
    d. 22.50 mL of a 0.025-*M* solution of $C_{12}H_{22}O_{11}$ is diluted to 100.0 mL
    Check Answer: [19]
21. What is the final concentration of the solution produced when 225.5 mL of a 0.09988-*M* solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?
22. A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution? **Check Answer:** [20]
23. An experiment in a general chemistry laboratory calls for a 2.00-*M* solution of HCl. How many mL of 11.9 *M* HCl would be required to make 250 mL of 2.00 *M* HCl?
24. What volume of a 0.20-*M* K_2SO_4 solution contains 57 g of K_2SO_4? **Check Answer:** [21]
25. The US Environmental Protection Agency (EPA) places limits on the quantities of toxic substances that may be discharged into the sewer system. Limits have been established for a variety of substances, including hexavalent chromium, which is limited to 0.50 mg/L. If an industry is discharging hexavalent chromium as potassium dichromate ($K_2Cr_2O_7$), what is the maximum permissible molarity of that substance?

14.4 – Other Units for Solution Concentrations

1. Consider this question: What mass of a concentrated solution of nitric acid (68.0% HNO_3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO_3 by mass?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
    Check Answer: [22]
2. What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?
3. What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.
    Check Answer: [23]

4. What mass of HCl is contained in 45.0 mL of an aqueous HCl solution that has a density of 1.19 g cm^{-3} and contains 37.21% HCl by mass?
5. The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $CaCO_3$, which is equivalent to milligrams of $CaCO_3$ per litre of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?
   Check Answer: [24]
6. The level of mercury in a stream was suspected to be above the minimum considered safe (1 part per billion by weight). An analysis indicated that the concentration was 0.68 parts per billion. Assume a density of 1.0 g/mL and calculate the molarity of mercury in the stream.
7. In Canada and the United Kingdom, devices that measure blood glucose levels provide a reading in millimoles per litre. If a measurement of 5.3 m*M* is observed, what is the concentration of glucose ($C_6H_{12}O_6$) in mg/dL?
   Check Answer: [25]
8. A throat spray is 1.40% by mass phenol, C_6H_5OH, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.
9. Copper(I) iodide (CuI) is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?
   Check Answer: [26]
10. A cough syrup contains 5.0% ethyl alcohol, C_2H_5OH, by mass. If the density of the solution is 0.9928 g/mL, determine the molarity of the alcohol in the cough syrup.
11. D5W is a solution used as an intravenous fluid. It is a 5.0% by mass solution of dextrose ($C_6H_{12}O_6$) in water. If the density of D5W is 1.029 g/mL, calculate the molarity of dextrose in the solution.
    Check Answer: [27]
12. Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid, H_2SO_4, for which the density is 1.3057 g/mL.

14.5 – Colligative Properties and Osmosis

1. Which is/are part of the macroscopic domain of solutions and which is/are part of the microscopic domain: boiling point elevation, Henry's law, hydrogen bond, ion-dipole attraction, molarity, nonelectrolyte, nonstoichiometric compound, osmosis, solvated ion?
2. What is the microscopic explanation for the macroscopic behaviour illustrated in Figure 14.2f in Chapter 14.2 Solubility?
   Check Answer: [28]
3. Sketch a qualitative graph of the pressure versus time for water vapour above a sample of pure water and a sugar solution, as the liquids evaporate to half their original volume.
4. A solution of potassium nitrate, an electrolyte, and a solution of glycerin ($C_3H_5(OH)_3$), a

nonelectrolyte, both boil at 100.3 °C. What other physical properties of the two solutions are identical?
Check Answer: [29]

5. What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
6. What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
    Check Answer: [30]
7. Calculate the mole fraction of each solute and solvent:
    a. 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
    b. 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
    c. 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
    d. 25 g of I_2 in 125 g of ethanol, C_2H_5OH
8. Calculate the mole fraction of each solute and solvent:
    a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0 °C
    b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
    c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
    d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$
    Check Answer: [31]
9. Calculate the mole fractions of methanol, CH_3OH; ethanol, C_2H_5OH; and water in a solution that is 40% methanol, 40% ethanol, and 20% water by mass. (Assume the data are good to two significant figures.)
10. What is the difference between a 1 *M* solution and a 1 *m* solution?
    Check Answer: [32]
11. What is the molality of phosphoric acid, H_3PO_4, in a solution of 14.5 g of H_3PO_4 in 125 g of water?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
12. What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
    Check Answer: [33]
13. Calculate the molality of each of the following solutions:
    a. 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
    b. 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection

   c. 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
   d. 25 g of I_2 in 125 g of ethanol, C_2H_5OH
14. Calculate the molality of each of the following solutions:
    a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0°C
    b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
    c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
    d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

    Check Answer: [34]
15. The concentration of glucose, $C_6H_{12}O_6$, in normal spinal fluid is $\frac{75\text{ mg}}{100\text{ g}}$. What is the molality of the solution?
16. A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3. Calculate the molality of the solution.

    Check Answer: [35]
17. Why does 1 mol of sodium chloride depress the freezing point of 1 kg of water almost twice as much as 1 mol of glycerin?
18. What is the boiling point of a solution of 115.0 g of sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water?
    a. Outline the steps necessary to answer the question
    b. Answer the question

    Check Answer: [36]
19. What is the boiling point of a solution of 9.04 g of I_2 in 75.5 g of benzene, assuming the I_2 is nonvolatile?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
20. What is the freezing temperature of a solution of 115.0 g of sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water, which freezes at 0.0 °C when pure?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.

    Check Answer: [37]
21. What is the freezing point of a solution of 9.04 g of I_2 in 75.5 g of benzene?
    a. Outline the steps necessary to answer the following question.
    b. Answer the question.
22. What is the osmotic pressure of an aqueous solution of 1.64 g of $Ca(NO_3)_2$ in water at 25 °C? The volume of the solution is 275 mL.
    a. Outline the steps necessary to answer the question.
    b. Answer the question.

    Check Answer: [38]

23. What is osmotic pressure of a solution of bovine insulin (molar mass, 5700 g mol^{-1}) at 18 °C if 100.0 mL of the solution contains 0.103 g of the insulin?
    a. Outline the steps necessary to answer the question.
    b. Answer the question.
24. What is the molar mass of a solution of 5.00 g of a compound in 25.00 g of carbon tetrachloride (bp 76.8 °C; K_b = 5.02 °C/*m*) that boils at 81.5 °C at 1 atm?
    a. Outline the steps necessary to answer the question.
    b. Solve the problem.
    Check Answer: [39]
25. A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by 3.66 °C. Calculate the molar mass of the compound.
26. A 1.0 *m* solution of HCl in benzene has a freezing point of 0.4 °C. Is HCl an electrolyte in benzene? Explain.
    Check Answer: [40]
27. A solution contains 5.00 g of urea, $CO(NH_2)_2$, a nonvolatile compound, dissolved in 0.100 kg of water. If the vapour pressure of pure water at 25 °C is 23.7 torr, what is the vapour pressure of the solution?
28. A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at −1.94 °C. Calculate the molar mass of the substance.
    Check Answer: [41]
29. Arrange the following solutions in order by their decreasing freezing points: 0.1 *m* Na_3PO_4, 0.1 *m* C_2H_5OH, 0.01 *m* CO_2, 0.15 *m* NaCl, and 0.2 *m* $CaCl_2$.
30. Calculate the boiling point elevation of 0.100 kg of water containing 0.010 mol of NaCl, 0.020 mol of Na_2SO_4, and 0.030 mol of $MgCl_2$, assuming complete dissociation of these electrolytes.
    Check Answer: [42]
31. How could you prepare a 3.08 *m* aqueous solution of glycerin, $C_3H_8O_3$? What is the freezing point of this solution?
32. A sample of sulfur weighing 0.210 g was dissolved in 17.8 g of carbon disulfide, CS_2 (K_b = 2.43 °C/*m*). If the boiling point elevation was 0.107 °C, what is the formula of a sulfur molecule in carbon disulfide?
    Check Answer: [43]
33. In a significant experiment performed many years ago, 5.6977 g of cadmium iodide in 44.69 g of water raised the boiling point 0.181 °C. What does this suggest about the nature of a solution of CdI_2?
34. Lysozyme is an enzyme that cleaves cell walls. A 0.100-L sample of a solution of lysozyme that contains 0.0750 g of the enzyme exhibits an osmotic pressure of 1.32×10^{-3} atm at 25 °C. What is the molar mass of lysozyme? **Check Answer:** [44]
35. The osmotic pressure of a solution containing 7.0 g of insulin per litre is 23 torr at 25 °C. What is the molar mass of insulin?
36. The osmotic pressure of human blood is 7.6 atm at 37 °C. What mass of glucose, $C_6H_{12}O_6$, is required

to make 1.00 L of aqueous solution for intravenous feeding if the solution must have the same osmotic pressure as blood at body temperature, 37 °C?
Check Answer: [45]

37. What is the freezing point of a solution of dibromobenzene, $C_6H_4Br_2$, in 0.250 kg of benzene, if the solution boils at 83.5 °C?
38. What is the boiling point of a solution of NaCl in water if the solution freezes at −0.93 °C?
Check Answer: [46]
39. The sugar fructose contains 40.0% C, 6.7% H, and 53.3% O by mass. A solution of 11.7 g of fructose in 325 g of ethanol has a boiling point of 78.59 °C. The boiling point of ethanol is 78.35 °C, and K_b for ethanol is 1.20 °C/m. What is the molecular formula of fructose?
40. The vapour pressure of methanol, CH_3OH, is 94 torr at 20 °C. The vapour pressure of ethanol, C_2H_5OH, is 44 torr at the same temperature.
    a. Calculate the mole fraction of methanol and of ethanol in a solution of 50.0 g of methanol and 50.0 g of ethanol.
    b. Ethanol and methanol form a solution that behaves like an ideal solution. Calculate the vapour pressure of methanol and of ethanol above the solution at 20 °C.
    c. Calculate the mole fraction of methanol and of ethanol in the vapour above the solution.
    Check Answer: [47]
41. The triple point of air-free water is defined as 273.15 K. Why is it important that the water be free of air?
42. Meat can be classified as fresh (not frozen) even though it is stored at −1 °C. Why wouldn't meat freeze at this temperature?
Check Answer: [48]
43. An organic compound has a composition of 93.46% C and 6.54% H by mass. A solution of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C. K_f for camphor is 37.7 °C/m. What is the molecular formula of the solute? Show your calculations.
44. A sample of $HgCl_2$ weighing 9.41 g is dissolved in 32.75 g of ethanol, C_2H_5OH (K_b = 1.20 °C/m). The boiling point elevation of the solution is 1.27 °C. Is $HgCl_2$ an electrolyte in ethanol? Show your calculations. **Check Answer:** [49]
45. A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about −1.4 °C. What is the formula of the salt? Show your calculations.

14.6 – Colloids

1. Identify the dispersed phase and the dispersion medium in each of the following colloidal systems: starch dispersion, smoke, fog, pearl, whipped cream, floating soap, jelly, milk, and ruby.
Check Answer: [50]

2. Distinguish between dispersion methods and condensation methods for preparing colloidal systems.
3. How do colloids differ from solutions with regard to dispersed particle size and homogeneity?
   Check Answer: [51]
4. Explain the cleansing action of soap.
5. How can it be demonstrated that colloidal particles are electrically charged?
   Check Answer: [52]

Attribution & References

Except where otherwise noted, this page is adapted by Gregory A. Anderson from "11.1 The Dissolution Process", "11.3 Solubility", "6.3 Molarity", "6.4 Other Units for Solution Concentrations", "11.4 Colligative Properties" and "11.5 Colloids" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* . / Extracted and reused review questions and solutions from end of pages.

Notes

1. A solution can vary in composition, while a compound cannot vary in composition. Solutions are homogeneous at the molecular level, while other mixtures are heterogeneous.
2. (a) The process is endothermic as the solution is consuming heat. (b) Attraction between the K^+ and $NO_3{}^-$ ions is stronger than between the ions and water molecules (the ion-ion interactions have a lower, more negative energy). Therefore, the dissolution process increases the energy of the molecular interactions, and it consumes the thermal energy of the solution to make up for the difference. (c) No, an ideal solution is formed with no appreciable heat release or consumption.
3. (a) ion-dipole forces; (b) dipole-dipole forces; (c) dispersion forces; (d) dispersion forces; (e) hydrogen bonding
4. Heat is released when the total intermolecular forces (IMFs) between the solute and solvent molecules are stronger than the total IMFs in the pure solute and in the pure solvent: Breaking weaker IMFs and forming stronger IMFs releases heat. Heat is absorbed when the total IMFs in the solution are weaker than the total of those in the pure solute and in the pure solvent: Breaking stronger IMFs and forming weaker IMFs absorbs heat.
5. The solubility of solids usually decreases upon cooling a solution, while the solubility of gases usually decreases upon heating.
6. 40%
7. 2.80 g
8. 2.9 atm
9. 102 L HCl
10. We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.
11. (a) 0.679 M; (b) 1.00 M; (c) 0.06998 M; (d) 1.75 M; (e) 0.070 M; (f) 6.6 M
12. (a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine

the mass of glucose from the number of moles and its molar mass; (b) 27 g

13. (a) 37.0 mol H_2SO_4; 3.63 × 10^3 g H_2SO_4; (b) 3.8 × 10^{-6} mol NaCN; 1.9 × 10^{-4} g NaCN; (c) 73.2 mol H_2CO; 2.20 kg H_2CO; (d) 5.9 × 10^{-7} mol $FeSO_4$; 8.9 × 10^{-5} g $FeSO_4$
14. (a) Determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity; (b) 1.15 × 10^{-3}*M*
15. (a) 5.04 × 10^{-3}*M*; (b) 0.499 *M*; (c) 9.92 *M*; (d) 1.1 × 10^{-3}*M*
16. 0.025 *M*
17. 0.5000 L
18. 1.9 mL
19. (a) 0.125 *M*; (b) 0.04888 *M*; (c) 0.206 *M*; (e) 0.0056 *M*
20. 11.9 *M*
21. 1.6 L
22. (a) The dilution equation can be used, appropriately modified to accommodate mass-based concentration units: $\%\text{mass}_1 \times \text{mass}_1 = \%\text{mass}_2 \times \text{mass}_2$ This equation can be rearranged to isolate mass_1 and the given quantities substituted into this equation. (b) 58.8 g
23. 114 g
24. 1.75 × 10^{-3}*M*
25. 95 mg/dL
26. 2.38 × 10^{-4} mol
27. 0.29 mol
28. The strength of the bonds between like molecules is stronger than the strength between unlike molecules. Therefore, some regions will exist in which the water molecules will exclude oil molecules and other regions will exist in which oil molecules will exclude water molecules, forming a heterogeneous region.
29. Both form homogeneous solutions; their boiling point elevations are the same, as are their lowering of vapour pressures. Osmotic pressure and the lowering of the freezing point are also the same for both solutions.
30. (a) Find number of moles of HNO_3 and H_2O in 100 g of the solution. Find the mole fractions for the components. (b) The mole fraction of HNO_3 is 0.378. The mole fraction of H_2O is 0.622.
31. (a) $X_{\text{Na}_2\text{CO}_3} = 0.0119$; $X_{\text{H}_2\text{O}} = 0.988$; (b) $X_{\text{NH}_4\text{NO}_3} = 0.9927$; $X_{\text{H}_2\text{O}} = 0.907$; (c) $X_{\text{Cl}_2} = 0.192$; $X_{\text{CH}_2\text{Cl}_2} = 0.808$; (d) $X_{\text{C}_5\text{H}_9\text{N}} = 0.00426$; $X_{\text{CHCl}_3} = 0.997$
32. In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.
33. (a) Determine the molar mass of HNO_3. Determine the number of moles of acid in the solution. From the number of moles and the mass of solvent, determine the molality. (b) 33.7 *m*
34. (a) 6.70 × 10^{-1}*m*; (b) 5.67 *m*; (c) 2.8 *m*; (d) 0.0358 *m*
35. 1.08 *m*
36. (a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the boiling point of water and the boiling point of the solution; determine the new boiling point. (b) 100.5 °C
37. (a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the freezing temperature of water and the freezing temperature of the solution; determine the new

freezing temperature. (b) −1.8 °C

38. (a) Determine the molar mass of $Ca(NO_3)_2$; determine the number of moles of $Ca(NO_3)_2$ in the solution; determine the number of moles of ions in the solution; determine the molarity of ions, then the osmotic pressure. (b) 2.67 atm
39. (a) Determine the molal concentration from the change in boiling point and K_b; determine the moles of solute in the solution from the molal concentration and mass of solvent; determine the molar mass from the number of moles and the mass of solute. (b) 2.1×10^2 g mol^{-1}
40. No. Pure benzene freezes at 5.5 °C, and so the observed freezing point of this solution is depressed by $\Delta T_f = 5.5 - 0.4 = 5.1$ °C. The value computed, assuming no ionization of HCl, is $\Delta T_f = (1.0\text{ m})(5.14\text{ °C}/m) = 5.1$ °C. Agreement of these values supports the assumption that HCl is not ionized.
41. 144 g mol^{-1}
42. 0.870 °C
43. S_8
44. 1.39×10^4 g mol^{-1}
45. 54 g
46. 100.26 °C
47. (a) $X_{CH_3OH} = 0.590$; $X_{C_2H_5OH} = 0.410$; (b) Vapor pressures are: CH_3OH: 55 torr; C_2H_5OH: 18 torr; (c) CH_3OH: 0.75; C_2H_5OH: 0.25
48. The ions and compounds present in the water in the beef lower the freezing point of the beef below −1 °C.
49. $\Delta\text{bp} = K_b m = (1.20\ {}^\circ\text{C}/m)\left(\dfrac{9.41\text{ g} \times \frac{1\text{ mol HgCl}_2}{271.496\text{ g}}}{0.03275\text{ kg}}\right) = 1.27\ {}^\circ\text{C}$ The observed change equals the theoretical change; therefore, no dissociation occurs.
50.

Colloidal System	Dispersed Phase	Dispersion Medium
starch dispersion	starch	water
smoke	solid particles	air
fog	water	air
pearl	water	calcium carbonate ($CaCO_3$)
whipped cream	air	cream
floating soap	air	soap
jelly	fruit juice	pectin gel
milk	butterfat	water
ruby	chromium(III) oxide (Cr_2O_3)	aluminum oxide (Al_2O_3)

51. Colloidal dispersions consist of particles that are much bigger than the solutes of typical solutions. Colloidal particles are either very large molecules or aggregates of smaller species that usually are big enough to scatter light. Colloids are homogeneous on a macroscopic (visual) scale, while solutions are homogeneous on a microscopic (molecular) scale.
52. If they are placed in an electrolytic cell, dispersed particles will move toward the electrode that carries a charge opposite to their own charge. At this electrode, the charged particles will be neutralized and will coagulate as a precipitate.

CHAPTER 15: REACTIONS IN AQUEOUS SOLUTIONS

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The properties of salts and give examples
- The properties of electrolytes and classifying them as strong or weak.
- Precipitation reactions in aqueous solutions

- Writing molecular equations, complete ionic equations, net ionic equations (for neutralization, precipitation, and gas formation reactions)
- Concepts relating to the ionization of water

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Nomenclature for ionic compounds: naming ionic compounds and writing its chemical formula
- How to use your scientific calculator including the following functions (buttons): scientific notation.
- Polyatomic ions
- Review double displacement reactions and balancing chemical equations
- Solubility concepts
- Properties of water

We have learned in the previous section(s) that solutions are of extreme importance in everyday life. The food we eat, the liquids we drink, the fluids in our body, the air we breathe, and the household products we use, such as household cleaners, hand sanitizers, and medications, are all solutions. We often focus on solutions only being table salt dissolving in water when, actually, particles like pollutants suspended in the air are also solutions. This particular example is a gaseous solution. Metal alloys, such as brass (which is mix of copper and zinc), is an example of a solid solution.

This chapter will focus on reactions occurring specifically in aqueous solutions. Water is by far the most important liquid solvent, partly because it is plentiful and partly because of its unique properties. In your body, in other living systems, and in the outside environment a tremendous number of reactions take place in aqueous solutions. Consequently this section, as well as significant portions of many other sections of this text, are devoted to developing an understanding of reactions which occur in water. Since ionic compounds and polar covalent compounds constitute the main classes which are appreciably soluble in water, reactions in aqueous solutions usually involve these types of substances. There are three important classes of reactions which occur in aqueous solution: precipitation reactions, acid-base reactions, and oxidation-reduction (redox) reactions.

- Precipitation reactions are useful for detecting the presence of various ions and for determining the concentrations of solutions.
- Acid-base reactions and redox reactions are similar in that something is being transferred from one species to another.
    - Acid-base reactions involve proton transfers, whereas redox reactions involve electron transfers.
    - Redox reactions are somewhat more complicated, though, because proton transfers and other bond-making and bond-breaking processes occur at the same time as electron transfer.

Below are demonstrations of each of the types of reactions. Some of these reactions will be explained in detail in this chapter; others will be covered in more depth in later chapters.

The first video demonstrates precipitation reaction between aqueous solutions of silver nitrate and sodium chloride.

Watch Double Displacement Reaction of $AgNO_3$ and NaCl (41 sec)

The next video demonstrates an acid and base reacting with aluminum (in the form of a soda can) at room temperature. When aluminum reacts with hydrochloric acid, it yields aqueous aluminum chloride and colourless hydrogen gas. When aluminum reacts with sodium hydroxide it forms water soluble sodium aluminate and hydrogen gas as products.

Watch Coke Cans in Acid and Base – Periodic Table of Videos (2min 49sec)

The last video shows a displacement reaction of zinc metal in aqueous copper (II) sulfate solution.

Watch Displacement Reaction of Metals – Zinc in Copper (II) Sulfate – with explanation at micro level (5min 45 sec).

Attribution & References

Except where otherwise noted, this section is adapted by Jackie MacDonald from “11.1: Prelude to Aqueous Phase Reactions” In *ChemPRIME (LibreTexts CHEMISTRY)* by Ed Vitz, John W. Moore, Justin Shorb, Xavier Prat-Resina, Tim Wendorff, & Adam Hahn, licensed under CC BY-NC-SA 4.0. / Adaptations and additions to content was updated for student comprehension.

15.1 SALTS

Learning Objectives

By the end of this section, you will be able to:

- Define the term salt and identify common salts
- Explain how a salt is formed

Salts are found all around us and within our human body. In nature, these ionic compounds are abundant in rocks and minerals of the Earth's mantel but also found in seawater and other bodies of water. We have already learned about salts when discussing ionic compounds. Salts are a chemical compound formed when ions form ionic bonds. In these reactions, one atom gives up one or more electrons, and thus becomes positively charged, whereas the other accepts one or more electrons and becomes negatively charged; overall the ionic compound has no net charge. Salts typically are crystalline, odourless, colourless/transparent or white, and have high melting and boiling points. As we learned in the previous chapter on solutions, many salts are soluble in water; however, some are not. If a given salt is soluble in water, it completely dissociates into ions other than a hydrogen ion (H^+) or hydroxide ion (OH^-) and forms an aqueous solution. This fact is elemental in distinguishing salts from acids and bases. Salts are derived from the neutralization reaction of an acid and base. Since acids and bases always contain either a metal cation or a cation derived from ammonium (NH_4^+) and a nonmetal anion, the two can combine to form a salt. For instance, when you mix aqueous solutions of hydrochloric acid and sodium hydroxide, aqueous sodium chloride and water are formed.

$$\mathrm{HCl(aq)+NaOH}(aq) \rightarrow \mathrm{NaCl}(aq)\mathrm{+H_2O}(l)$$

If the aqueous solution of sodium chloride undergoes a distillation process, a solid, crystalline NaCl salt would remain. Concepts related to acids and bases will be discussed in more detail in the next chapter.

A common salt, NaCl, also known as table salt, dissociates completely in water (Figure 15.1a). The positive and negative regions on the water molecule (the hydrogen and oxygen ends respectively) attract the negative chloride and positive sodium ions, pulling them away from each other. Non-polar and polar covalently bonded compounds break apart into molecules in solution; however, salts dissociate into ions. These ions are electrolytes, which will be discussed in the next section. This ionic property is critical to the function of ions in the human body when transmitting nerve impulses and prompting muscle contraction.

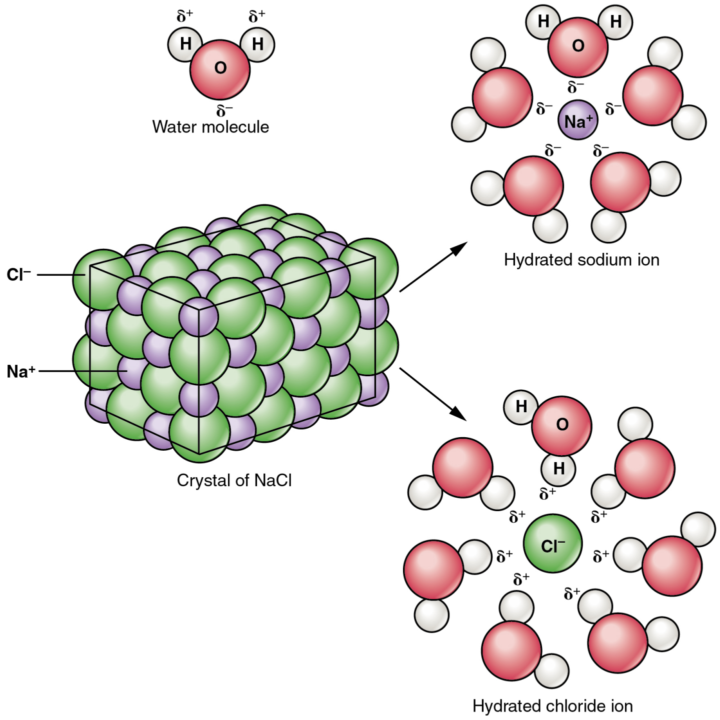

Figure 15.1a Dissociation of Sodium Chloride in Water: Notice that the solid crystals of sodium chloride dissociate not into molecules of NaCl, but into Na^+ cations and Cl^- anions, each completely surrounded by water molecules (credit: *Anatomy and Physiology 2e (Open Stax)*, CC BY 4.0)

Many other salts are important in the body. For example, bile salts produced by the liver help break apart dietary fats, and calcium phosphate salts, $Ca_3(PO_4)_2$ (*s*), form the mineral portion of teeth and bones. Some other commons salts include:

- Na_2CO_3 (sodium bicarbonate): Baking soda
- $MgSO_4$ – (magnesium sulfate): Epsom salt
- Fe_2O_3 (iron (III) oxide): Rust
- KNO_3 (potassium nitrate): component of crop fertilizer, used in rocket propellants, fireworks, gunpowder

Indigenous Perspective: Bone

Bone has two components: organic matter (which is mostly Type I collagen) and about 70% inorganic matter. The inorganic material of bone consists of calcium phosphate mineral crystals known as hydroxyapatite, $Ca_5(PO_4)_3(OH)$. This mineral is embedded throughout the organic bone matrix to give bone its structural stability and strength.

One of the composite materials traditionally important to Inuit has been bone. This comes from a variety of natural sources, including caribou antler and walrus tusk. An important use of this strong carvable material is in snow goggles, called *ilgaak* or *iggaak*. Wearing these human-made goggles are invaluable in preventing snow blindness (Rayner-Canham et al., 2016, Composite Materials section).

Figure 15.1b Ilgaak/Iggaak – Inuit snow goggles: Snow goggles such as the ones illustrated are commonly made from caribou antler with caribou sinew for a strap (credit: work by CambridgeBayWeather, PD)

Not only are salts crucial compounds necessary for sustaining life, but they are also invaluable constituents of chemical reactions that occur around us on a daily basis.

Watch What are Salts? (5min 9s).

Attribution & References

Except where otherwise noted, this section is adapted by Jackie MacDonald from "2.4 Inorganic Compounds Essential to Human Functioning" In *Anatomy and Physiology 2e (Open Stax)* by J. Gordon Betts, Kelly A. Young, James A. Wise, Eddie Johnson, Brandon Poe, Dean H. Kruse, Oksana Korol, Jody E. Johnson, Mark

References

Rayner-Canham, G., Taylor, R., & Lee, Y.-R. (2016, February). *Making chemistry relevant to Indigenous Peoples*. Chem 13 News Magazine. Retrieved December 15, 2022, from https://uwaterloo.ca/chem13-news-magazine/february-2016/feature/making-chemistry-relevant-indigenous-peoples

15.2 ELECTROLYTES

Learning Objectives

By the end of this section, you will be able to:

- Define electrolyte and give examples of electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

Pure water (purified water) is a pure substance made up of just three atoms: two hydrogen and one oxygen atom, H_2O. Since pure water has no constituents other than these atoms, it does not have any taste or smell, and it doesn't conduct electricity on its own. However, water can become a medium for conducting electricity. When ionic substances (salts) are dissolved in water, they undergo either a physical or a chemical change that yields free ions moving independently in the aqueous solution. This feature permits them to carry positive or negative electrical charges from one place to another and the solution can conduct an electrical current. These substances constitute an important class of compounds called **electrolytes**. Salts that ionize in aqueous solution are great conductors of electricity and are known as electrolytes. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a **weak electrolyte**.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 15.2a).

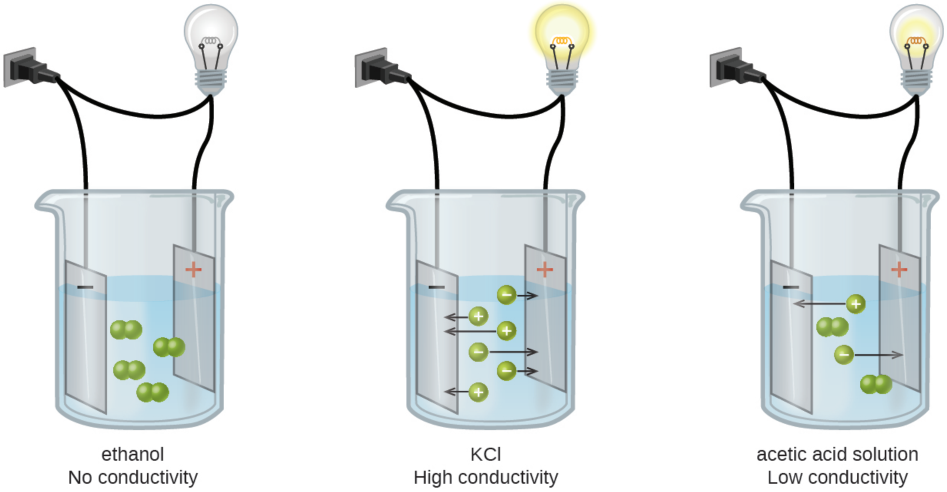

Figure 15.2a Solutions Containing Nonelectrolytes, Strong Electrolytes, or Weak Electrolytes: Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 15.2b. The electrostatic attraction between an ion and a molecule with a dipole is called an **ion-dipole attraction**. These attractions play an important role in the dissolution (ionization) of ionic compounds in water.

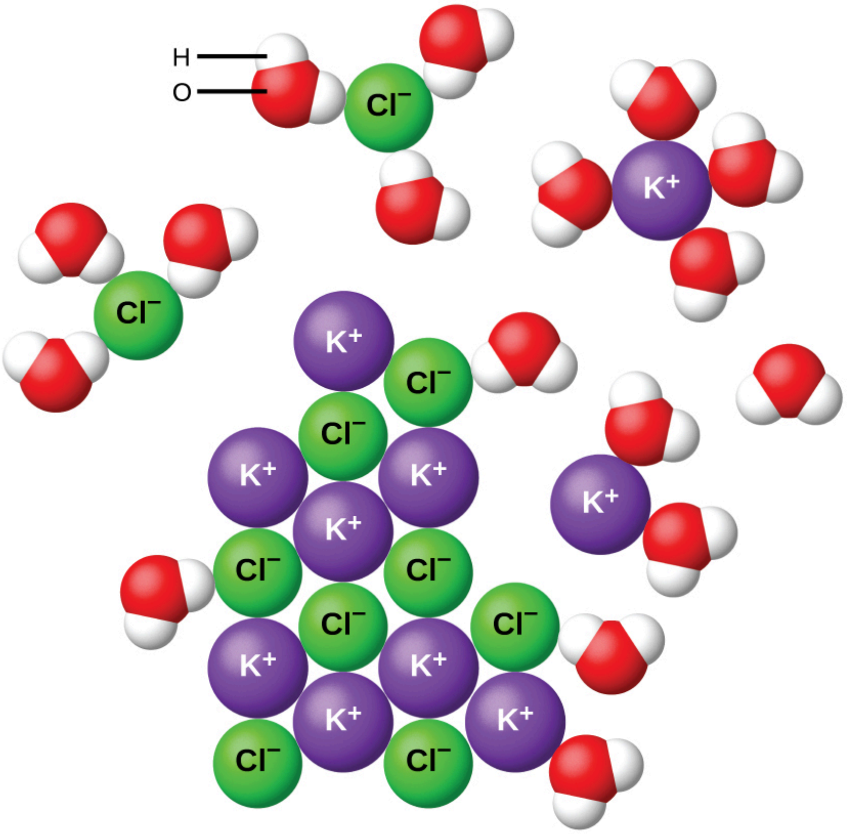

Figure 15.2b Representation of what Happens when Potassium Chloride is Dissolved in Water: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as **dissociation**, which was discussed in the previous chapter – Solutions. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure 15.2b shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with the absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for salt compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Covalent Electrolytes

As mentioned previously, pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. The ionization of water will be discussed in more depth later in this chapter and these concepts will be important in understanding the behaviours of acids and bases. In brief, water ionizes when one molecule of water gives up a proton to another molecule of water, yielding hydronium and hydroxide ions.

$$\mathrm{H_2O}(l) \ + \ \mathrm{H_2O}(l) \leftrightharpoons \mathrm{H_3O^+}(aq) \ + \ \mathrm{OH^-}(aq)$$

In some cases, we find that solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalently bonded HCl molecules. This gas contains no ions. Hydrogen chloride gas is very soluble in water and is dissolved in water to prepare hydrochloric acid. When we dissolve hydrogen chloride gas in water, we find that the solution is a very good conductor. The water molecules play an essential part in forming ions. However, it is important to note that solutions of hydrogen chloride in many other solvents, such as benzene, do not conduct electricity and do not contain ions.

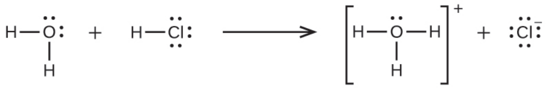

Figure 15.2c Reaction between Water and Hydrogen Chloride Gas to form Hydrochloric Acid: Hydrogen chloride gas dissolves in water and the ions react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-), which illustrates the ionization of this strong acid (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Hydrogen chloride gas dissolves in water and the ions react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-). This illustrates the ionization of a strong acid.

This reaction is essentially 100% complete for HCl (i.e., it is a strong acid and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. You will learn more about classifying the strength of acids and bases in later chapters.

For a summary **Watch** **Aqueous Solutions, Dissolving, and Solvation (14min 6sec).**

Attribution & References

Except where otherwise noted, this page is adapted by Jackie MacDonald from "11.2 Electrolytes" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*. / Adaptations and additions were made to content in this section were made or student comprehension.

15.3 PRECIPITATION REACTIONS

Learning Objectives

By the end of this section, you will be able to:

- Predict the solubility of common inorganic compounds by using solubility rules
- Define precipitation reactions
- Recognize and identify examples of precipitation reactions
- Apply the solubility rules of common inorganic compounds to predict the products formed when two aqueous solutions are mixed

Scientists have found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This section of this chapter will focus on a specific type of double displacement reaction called a precipitation reaction.

Precipitation Reactions and Solubility Rules

Solubility of Inorganic Compounds

The idea of solubility was introduced in the solutions chapter. The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its **solubility**, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be **soluble** and are found as dissolved ions in aqueous solution. A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be **insoluble**, and these are the substances that readily precipitate from solution to form a solid (*s*). For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to the solubility guidelines for many ionic compounds in Table 15.3a to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. First, it is important to become familiar with using the solubility table to determine if a given salt will dissolve (*aq*), or not (*s*) in aqueous solution. If a salt is said to be insoluble, or has low solubility, or is slightly soluble, it will form a precipitate – a solid – and the symbol (*s*) will be used to represent that observation. If a salt is soluble, the salt will dissociate (ionize) in aqueous solution, and the symbol (*aq*) will be used to show that chemistry. It is important to mention that Table 15.3a does not include every possible soluble, insoluble salt combination. Since there are other possibilities, Table 14.2a and Table 14.2b can also be referenced to determine solubility of inorganic compounds.

Table 15.3a Solubility Guidelines for Inorganic Compounds in Water at 25°C

Negative Ion (Anion)	Positive Ion (Cation)	Solubility	Phase, Phase Symbol
All	Li^+, Na^+, K^+, Rb^+, Cs^+ NH_4^+	Soluble	aqueous, (*aq*)
Chloride (Cl^-), Bromide (Br^-), Iodide (I^-)	Ag^+, Pb^{2+}, Hg_2^{2+}, Cu^+	Low solubility	solid, (*s*)
Chloride (Cl^-), Bromide (Br^-), Iodide (I^-)	All others	Soluble	aqueous, (*aq*)
F^-	compounds with group 2 metal cations, Li^+, Al^{3+}, Pb^{2+}, $Fe^{2+}$and Fe^{3+}	Low solubility	solid, (*s*)
F^-	All others	Soluble	aqueous, (*aq*)
Hydroxide (OH^-)	Li^+, Na^+, K^+, Rb^+, NH_4^+, Sr^{2+}, Ba^{2+}	Soluble	aqueous, (*aq*)
Hydroxide (OH^-)	All others	Low solubility	solid, (*s*)
NO_3^-, NO_2^-	All (exception: $AgNO_2$ is insoluble)	Soluble	aqueous, (*aq*)
Phosphate (PO_4^{3-}), Carbonate (CO_3^{2-})	Na^+, K^+, Rb^+, NH_4^+	Soluble	aqueous, (*aq*)
Phosphate (PO_4^{3-}), Carbonate (CO_3^{2-})	All others	Low solubility	solid, (*s*)
Sulphate (SO_4^{2-})	Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Pb^{2+}	Low solubility	solid, (*s*)
Sulphate (SO_4^{2-})	All others	Soluble	aqueous, (*aq*)

Source: "Table 15.3a Solubility Guidelines for Inorganic Compounds in Water at 25°C" was created by Jackie MacDonald, CC BY-NC-SA 4.0.

Using the Solubility Table Guidelines to Determine Solubility

To qualitatively determine the solubility of a salt in aqueous solution, reference Table 15.3a and follow the steps outline below:

1. Identify the negative ion in the salt; locate the ion in the first column of Table 15.3a.
2. Determine the positive ion in the salt by moving into the second column, same row as your anion.
3. Finally, move horizontally in that row into the solubility column (column 3) to determine whether that compound is soluble or insoluble.
4. Identify the symbol used to represent its solubility

Example 15.3a

Use the solubility rules to determine the solubility of the following substances. Categorize each as soluble or insoluble and also write the symbol used to show its solubility.

1. Na_2S
2. AgBr
3. $Mg(Cl)_2$

Solution

1. Soluble, (*aq*) – Since S is not listed as an anion, it falls into the "all" option. It's cation is a Na^+ cation, so it is soluble, *aq*.
2. Insoluble, (*s*) – When Br^- forms a salt with Ag^+, it forms an insoluble salt, *s*.
3. Soluble, (*aq*) – When Cl^- forms a salt with Mg^{2+}, it fall into the "all others" category for cations, and it forms a soluble salt, *aq*.

Source: Example 15.3a created by Jackie MacDonald and David McCuaig, CC BY-NC-SA 4.0.

Exercise 15.3a

Check Your Learning Exercise (Text Version)
From the options provided, identify the salts that will form a precipitate in aqueous solution at 25 degrees Celsius.

1. $Fe(NO_3)_2$
2. $BaSO_4$
3. AgF
4. $Mg(OH)_2$

5. $AgNO_2$
6. $ZnCl_2$
7. PbI_2
8. KBr
9. $LiClO_3$
10. AgBr
11. KOH
12. $(NH_4)PO_4$
13. $CaCO_3$

Check Your Answers[1]

Source: "Exercise 15.3a" created by Jackie MacDonald and David McCuaig, licensed under CC BY-NC-SA 4.0.

Watch the video Precipitation Reactions starting at 6min 31sec until 9min05sec. It demonstrates how to use a similar solubility table to determine solubility.

For a more in depth solubility table that is online and printable, link to "Solubility Rules Chart" by MilliporeSigma.

Source: Section titled "How to Use the Solubility Table Guidelines to Determine Solubility" was created by Jackie MacDonald and David McCuaig and is licensed under CC BY-NC-SA 4.0.

Precipitation Reactions

A **precipitation reaction** is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as double displacement, double replacement, or metathesis reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and gravimetric methods for determining the composition of matter.

A vivid example of precipitation is observed when aqueous solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

$$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts. Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 15.3a). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.

Figure 15.3a Formation of Precipitate Lead(II) Iodide during a Precipitation Reaction: The precipitation reaction producing Lead(II) iodide is shown. It is known as "golden rain" because of the yellow hexagonal crystals forming throughout in the aqueous solution and the solid crystals settle at the bottom of the beaker. This picture was taken after cooling a heated lead(II) nitrate and potassium iodide solution on a Bunsen burner. (credit: work by Der Kreole, CC BY-SA 3.0)

The solubility table may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound.

For example, mixing aqueous solutions of silver nitrate and sodium chloride will yield a solution containing Ag^+, NO_3^-, Na^+, and Cl^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaCl, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgCl. The solubility table can be used to determine if either of these salt combinations are insoluble in aqueous solution. Insoluble salts will precipitate out of the solution to form a solid (*s*).

The solubility table indicates all nitrate salts are soluble, so sodium nitrate ($NaNO_3$) will remain ions in solution. However, silver chloride, AgCl, is one of the exceptions to the general solubility rules of chloride salts, and this combination of ions will form a solid in aqueous solution. Therefore, a precipitation reaction is predicted to occur, as described by the following molecular equation:

$$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

Watch Precipitation Reactions (10mins 13sec).

Example 15.3b

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If a reaction occurs and a precipitation is expected, write a balanced molecular equation for the following two reactions.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate)

Solution

a. The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate KNO_3 is soluble and $BaSO_4$ is insoluble, so a precipitation reaction is expected. The balanced molecular equation for this reaction is $K_2SO_4(aq) + Ba(NO_3)_2\ (aq) \rightarrow BaSO_4(s) + 2KNO_3(aq)$
b. The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate $LiC_2H_3O_2$ is soluble and AgCl is insoluble, and so a precipitation reaction is expected. The balanced molecular equation for this reaction is $LiCl\ (aq) + AgC_2H_3O_2(aq) \rightarrow AgCl(s) + LiC_2H_3O_2(aq)$

Exercise 15.3b

Predict the result of mixing reasonably concentrated aqueous solutions of the following ionic compounds. If a reaction occurs and a precipitation is expected, write a balanced molecular equation for the following reaction between lead(II) nitrate and ammonium carbonate.

Check Your Answer[2]

Exercise 15.3c

Which solution(s) could be used to precipitate the barium ion, Ba^{2+}, in a aqueous solution barium nitrate: sodium chloride, sodium hydroxide, or sodium sulfate? If a reaction occurs and a precipitation is expected, write a balanced molecular equation for that reaction

Check Your Answer[3]

Links to Interactive Learning Tools

Explore Precipitation Reactions from the Physics Classroom.

Attribution & References

Except where otherwise noted, this page is adapted by Jackie MacDonald from "6.2 Precipitation Reactions" In *CHEM 1114 – Introduction to Chemistry (BCcampus, Pressbooks)* by Shirley Wacowich-Sgarbi and Langara

Notes

1. The salts that form precipitates are PbI_2, $AgBr$, $CaCO_3$, $Mg(OH)_2$, $BaSO_4$, $AgNO_2$
2. The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate NH_4NO_3 is soluble and $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The balanced molecular equation for this reaction is $Pb(NO_3)_2(aq) + (NH_4)_2CO_3(aq) \rightarrow PbCO_3(s) + 2NH_4NO_3(aq)$
3. The solubility table can be used to determine which ionic compounds containing barium will be insoluble in aqueous solution. There are three possibilities to consider: $BaCl_2$, $Ba(OH)_2$, and $BaSO_4$. The solubility guidelines indicate $BaCl_2$ and $Ba(OH)_2$ are soluble in water and will not form a precipitate; however, $BaSO_4$ is insoluble, so this combination will result in a precipitation reaction. The balanced molecular equation for this reaction is

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

15.4 DESCRIBING REACTIONS IN SOLUTIONS BY WRITING MOLECULAR, COMPLETE IONIC, AND NET IONIC EQUATIONS

Learning Objectives

By the end of this section, you will be able to:

- Write and balance chemical equations in molecular, complete ionic, and net ionic formats.

Ionic Compounds in Solution

We have learned that one important aspect about ionic compounds that differs from molecular compounds has to do with dissolving in a liquid, such as water. When molecular compounds, such as sugar, dissolve in water, the individual molecules drift apart from each other. When ionic compounds dissolve, the ions physically separate from each other. We can use a chemical equation to represent this process—for example, with NaCl:

$$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq)$$

Figure 15.4a Chemical Equation Illustrating Sodium Chloride Salt Ionizing in Water: NaCl will dissolve in water; each atom separates into their individual ions in the water solution. Na^+ and Cl^- ions disperse throughout the water and the salt has dissolved or ionized in the aqueous solution. (credit: work by Shirley Wacowich-Sgarbi, CC BY-NC-SA 4.0; / Adapted by Jackie MacDonald).

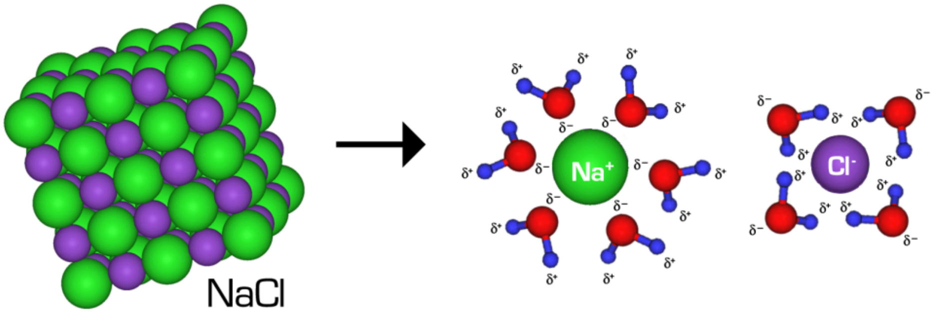

Figure 15.4b Water Hydration of a Crystal of Salt (NaCl): When immersed in water, the attractive forces of the water molecules to the NaCl separates the NaCl molecule to disperse into its separate ions. The negatively-charged oxygens of the water molecules are attracted to the positively-charged sodium ions. The positively-charged side of the water molecules (the hydrogen atoms) are attracted to the negatively-charged chloride ions. Water molecules pull the sodium and chloride ions apart, breaking the ionic bond that held them together. After the salt compounds are pulled apart, the sodium and chloride atoms are surrounded by water molecules. Once this happens, the salt is dissolved, resulting in a homogeneous solution. (credit: work by Andrea Hazard, CC-BY-SA 4.0)

When NaCl dissolves in water, the ions separate and go their own way in solution; the ions are now written with their respective charges, and the (aq) phase label emphasizes that they are dissolved (Figure 15.4a and Figure 15.4b). When an ionic compound dissociates in water, water molecules surround each ion and separate it from the rest of the solid. Each ion goes its own way in solution.

All ionic compounds that dissolve behave this way. (This behaviour was first suggested by the Swedish chemist Svante August Arrhenius [1859–1927] as part of his PhD dissertation in 1884. Interestingly, his PhD examination team had a hard time believing that ionic compounds would behave like this, so they gave Arrhenius a barely passing grade. Later, this work was cited when Arrhenius was awarded the Nobel Prize in Chemistry.)

Keep in mind that when the ions separate, *all* of the ions separate. Thus, when $CaCl_2$ dissolves, the one Ca^{2+} ion and the two Cl^- ions separate from each other:

$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + Cl^-(aq) + Cl^-(aq)$$

which is simplified to

$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

That is, the two chloride ions go off on their own. They do not remain as Cl_2 (that would be elemental chlorine; these are chloride ions); they do not stick together to make Cl_2^- or Cl_2^{2-}. They become dissociated ions in their own right. It is important to note that polyatomic ions retain their overall identity when they are dissolved. It is important to understand and write the chemical equation that represents the dissociation of ions, as it is a crucial concept when writing complete ionic chemical equations, and net ionic equations.

Example 15.4a

Write the chemical equation that represents the dissociation of each ionic compound.

a. KBr
b. Na_2SO_4
c. $(NH_4)_3PO_4$

Solution

a. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$
b. Not only do the two sodium ions go their own way, but the polyatomic sulfate ion stays together as the sulfate ion. The dissolving equation is $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$
c. Not only do the three ammonium ions stay together, but the one phosphate ion stays together as well since they are both polyatomic ions. The dissolving equation is $(NH_4)_3PO_4(s) \rightarrow 3NH_4^+(aq) + PO_4^{3-}(aq)$

Exercise 15.4a

Exercise 15.4a.1

1) Write the chemical equation that represents the dissociation of $(NH_4)_2S$.

Check Your Answer[1]

Exercise 15.4a.2

2) Write the chemical equation that represents the dissociation of iron(III) sulfate, $Fe_2(SO_4)_3$.

Check Your Answer[2]

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a precipitation reaction takes place producing aqueous $Ca(NO_3)_2$ and solid AgCl as shown in the following molecular equation:

$$CaCl_2(aq) + 2AgNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2AgCl(s)$$

This balanced equation, derived by means describe in previous sections, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may dissociate into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution. Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$
$$2AgNO_3(aq) \rightarrow 2Ag^+(aq) + 2NO_3^-(aq)$$
$$Ca(NO_3)_2(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$Ca^{2+}(aq) + 2Cl^{-}(aq) + 2Ag^{+}(aq) + 2NO_3^{-}(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^{-}(aq) + 2AgCl(s)$$

NOTE: the order in which the products are written, does not matter. The solid may be written first or second. Examining this complete ionic equation shows that two chemical species are present in identical forms on both sides of the arrow, $Ca^{2+}(aq)$ and $NO_3^{-}(aq)$. These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more concise representation called a **net ionic equation**. The net ionic equation summarizes the chemical change that occurred in the chemical reaction. Below, the complete ionic equation is shown first. The spectator ions ($Ca^{2+}(aq)$ and $2NO_3^{-}(aq)$) are bolded in blue. Then, the other reactants and products are included in the net ionic equation, which is shown second.

Complete Ionic Equation: $\mathbf{Ca^{2+}(aq)} + 2Cl^{-}(aq) + 2Ag^{+}(aq) + \mathbf{2NO_3^{-}(aq)} \rightarrow \mathbf{Ca^{2+}(aq)} + \mathbf{2NO_3^{-}(aq)} + 2AgCl(s)$

Net Ionic Equation: $2Cl^{-}(aq) + 2Ag^{+}(aq) \rightarrow 2AgCl(s)$

which can be simplified to the smallest possible integers as coefficients and written as

$$Cl^{-}(aq) + Ag^{+}(aq) \rightarrow AgCl(s)$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^{-} and Ag^{+}. The above reaction is a precipitation reaction.

Watch How to Write and Balance Net Ionic Equations (6min 18sec).

Example 15.4b

The molecular equations for two chemical reactions are given below: Write the complete ionic equation for each chemical reaction.

a. $KBr(aq) + AgC_2H_3O_2(aq) \rightarrow KC_2H_3O_2(aq) + AgBr(s)$
b. $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Solution

For any ionic compound that is aqueous, we will write the compound as separated ions.

a. The complete ionic equation is
   $K^{+}(aq) + Br^{-}(aq) + Ag^{+}(aq) + C_2H_3O_2^{-}(aq) \rightarrow K^{+}(aq) + C_2H_3O_2^{-}(aq) + AgBr(s)$
b. The complete ionic equation is

$Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Exercise 15.4b

Write the complete ionic equation for the following chemical chemical reaction:

$$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$$

Check Your Answer[3]

Example 15.4c

Write the net ionic equation for each chemical reaction below. Identify the spectator ions in each of these reactions.

a. $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
b. $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2\ NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2\ NO_3^-(aq) + BaSO_4(s)$

Solution

a. In the first equation, the $K^+(aq)$ and $C_2H_3O_2^-(aq)$ ions are spectator ions (bolded in blue), so they are cancelled.
   $\mathbf{K^+(aq)} + Br^-(aq) + Ag^+(aq) + \mathbf{C_2H_3O_2^-(aq)} \rightarrow \mathbf{K^+(aq)} + \mathbf{C_2H_3O_2^-(aq)} + AgBr(s)$;
   The net ionic equation is
   $Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$
b. In the second equation, the $Mg^{2+}(aq)$ and $NO_3^-(aq)$ ions are spectator ions (bolded in blue), so they are cancelled.
   $\mathbf{Mg^{2+}(aq)} + SO_4^{2-}(aq) + Ba^{2+}(aq) + \mathbf{2NO_3^-(aq)} \rightarrow \mathbf{Mg^{2+}(aq)} + \mathbf{2NO_3^-(aq)} + BaSO_4(s)$;
   The net ionic equation is
   $SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

Exercise 15.4c

Write the net ionic equation for the chemical reaction below. Identify the spectator ions in this reaction.

$Ca^{2+}(aq) + 2Cl^{-}(aq) + Pb^{2+}(aq) + 2NO_3^{-}(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^{-}(aq) + PbCl_2(s)$

Check Your Answer[4]

Example 15.4d

When aqueous barium chloride is mixed with an aqueous solution of sodium sulfate, the mixture reacts to yield solid barium sulfate and aqueous sodium chloride. Write balanced molecular, complete ionic, and net ionic equations for this process. Name the spectator ions.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + NaCl(aq)$ (unbalanced equation)

Balance is achieved easily in this case by changing the coefficient for NaCl to 2, resulting in the molecular equation for this reaction:

$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$ (balanced equation)

The dissolved ionic compounds, $BaCl_2$, Na_2SO_4, and NaCl, can be represented as dissociated ions to yield the complete ionic equation:

$Ba^{2+}(aq) + 2Cl^{-}(aq) + 2Na^{+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + 2Na^{+}(aq) + 2Cl^{-}(aq)$

Finally, identify the spectator ion(s), in this case $Na^{+}(aq)$ and $Cl^{-}(aq)$, and remove them from each side of the equation to generate the net ionic equation:

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

Exercise 15.4d

When an aqueous solution of $AgNO_3$ is added to an aqueous solution of $CaCl_2$, insoluble AgCl precipitates. Write three equations (complete molecular equation, complete ionic equation, and net ionic equation) that describe this process.

Check Your Answer[5]

Net Ionic Equations of Gas Forming Reactions

Sometimes a gas will be involved as one of the reactants or products in a solution reaction. Net ionic equations can be written for these chemical reactions, as well. For example,

$$2HCl(aq) + Na_2S(aq) \rightarrow H_2S(g) + 2NaCl(aq)$$

In this example, since hydrochloric acid fully dissociates in aqueous solution, the complete ionic equation would be:

$$2H^+(aq) + 2Cl^-(aq) + 2Na^+(aq) + S^{2-}(aq) \rightarrow H_2S(g) + 2Na^+(aq) + 2Cl^-(aq)$$

Removing the spectator ions we obtain the net ionic equation:

$$2H^+(aq) + S^{2-}(aq) \rightarrow H_2S(g)$$

Exercise 15.4e

When carbon dioxide gas combines with an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Check Your Answer[6]

Net Ionic Equations of Single Replacement Reactions

Involving Aqueous Solutions

Recall, that during a **single replacement reaction** (SR) there is an exchange of elements; typically cations; an element becomes a compound and a compound becomes an element. SR reactions are always oxidation reduction (redox) reactions. These types of reactions will be discussed more in the Oxidation Reduction chapter, but we will cover the basics of writing net ionic equations for redox reactions undergoing single replacement.

Consider the following SR reaction between iron metal and copper(II) nitrate:

$$\text{Balanced Molecular Equation: } Fe(s) + Cu(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Cu(s)$$

$$\text{Complete Ionic Equation: } Fe(s) + Cu^{2+}(aq) + 2NO_3^-(aq) \rightarrow Fe^{2+}(aq) + 2NO_3^-(aq) + Cu(s)$$

Since nitrate ions are dissociated in the reactant and product side of the complete ionic equation, these are removed to produce the net ionic equation.

$$\text{Net Ionic Equation: } Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$$

Exercise 15.4f

Write the complete ionic and net ionic equations for the following chemical reaction.

$Ni(s) + 2HCl(aq) \rightarrow NiCl_2(aq) + H_2(g)$

Check Your Answer[7]

Net Ionic Equations of Neutralization Reactions

A **neutralization reaction** is a type of double displacement/replacement reaction. There is a double exchange of two cations, or two anions to form two new compounds. Neutralization reactions will be discussed more in the Acids and Bases chapter, but we will cover the basics of writing net ionic equations for neutralization reactions, now. In a neutralization reaction, the reactants are an acid and a base, and the products are often a salt (soluble or insoluble) and water, and neither reactant is the water itself:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

Consider the following reaction between a strong acid, hydrochloric acid, and strong base, sodium hydroxide. The balanced molecular equation can be used to generate a complete ionic equation, and its net ionic equation:

$$\text{Balanced Molecular Equation: } HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Complete Ionic Equation: $H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$

Since nitrate ions are dissociated in the reactant and product side of the complete ionic equation, these are removed to produce the net ionic equation.

Net Ionic Equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Links to Interactive Learning Tools

Explore Net Ionic Equations from the Physics Classroom.

Attribution & References

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Notes

1. $(NH_4)_2S\ (s) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$
2. $Fe_2(SO_4)_3\ (s) \rightarrow 2Fe^{3+}(aq) + 3SO_4^{2-}(aq)$
3. Complete ionic equation is $Ca^{2+}(aq) + 2Cl^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + PbCl_2(s)$
4. $Ca^{2+}(aq)$ and $NO_3^-(aq)$ ions are spectator ions (bolded in blue), so they are cancelled. **$Ca^{2+}(aq)$** + $2Cl^-(aq)$ + $Pb^{2+}(aq)$ + **$2NO_3^-(aq)$** → **$Ca^{2+}(aq)$** + **$2NO_3^-(aq)$** + $PbCl_2(s)$; The net ionic equation is $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$
5. Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form: $AgNO_3(aq) + CaCl_2(aq) \rightarrow AgCl(s) + Ca(NO_3)_2(aq)$ (unbalanced equation) Balancing this reaction results in the molecular equation for this reaction: $2AgNO_3(aq) + CaCl_2(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$ (balanced equation) The dissolved ionic compounds, $AgNO_3$, $CaCl_2$, and $Ca(NO_3)_2$, can be represented as dissociated ions to yield the complete ionic equation: $2Ag^+(aq) + 2NO_3^-(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \rightarrow 2AgCl(s) + Ca^{2+}(aq) + 2NO_3^-(aq)$ Finally, identify the spectator ion(s), in this case $Ca^{2+}(aq)$ and $NO_3^-(aq)$, and remove them from each side of the equation to generate the net ionic equation: $2Ag^+(aq) + 2Cl^-(aq) \rightarrow 2AgCl(s)$ which can be simplified to the smallest possible integers as coefficients and written as $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
6. Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form: $CO_2(g) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ (unbalanced) Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction: $CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ (balanced) The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as

dissociated ions to yield the complete ionic equation: $CO_2(g) + 2Na^+(aq) + 2OH^-(aq) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq) + H_2O(l)$ Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation: $CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$ To review a video of this solution watch **How to Write the Net Ionic Equation for NaOH + CO_2 = Na_2CO_3 + H_2O (2mins 38sec).**

7. Complete Ionic Equation: $Ni(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Ni^{2+}(aq) + 2Cl^-(aq) + H_2(g)$ Since chloride ions are dissociated in both the reactant and product side of the complete ionic equation, these are removed to produce the net ionic equation.

   Net Ionic Equation: $Ni(s) + 2H^+(aq) \rightarrow Ni^{2+}(aq) + H_2(g)$

CHAPTER 15 - SUMMARY

15.1 Salts

Salts are a chemical compound formed when ions form ionic bonds. In these reactions, one atom gives up one or more electrons, and thus becomes positively charged, whereas the other accepts one or more electrons and becomes negatively charged; overall the ionic compound has no net charge. Salts typically are crystalline, odourless, colourless/transparent or white, and have high melting and boiling points. Many salts are soluble in water; however, some are not. If a given salt is soluble in water, it completely dissociates into ions other than a hydrogen ion (H^+) or hydroxide ion (OH^-) and forms an aqueous solution. This fact is elemental in distinguishing salts from acids and bases. Salts are derived from the neutralization reaction of an acid and base. Since acids and bases always contain either a metal cation or a cation derived from ammonium (NH_4^+) and a nonmetal anion, respectively, the two can combine to form a salt.

15.2 Electrolytes

Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes, while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

15.3 Precipitation Reactions

Chemical reactions are classified according to similar patterns of behaviour. Precipitation is one type of chemical reaction which involves the formation of one or more insoluble products. Precipitation reactions, also called double displacement reactions can be summarized with the following reaction equation:

$AB(aq) + CD\ (aq) \rightarrow AD(s) + CB(aq)$ or (s)

The formation of the solid from combining two aqueous solutions is the DRIVING FORCE of the reaction (the factor that makes the reaction go). A precipitation reaction can be predicted to occur with the help of a solubility table.

15.4 Describing Reactions in Solutions by Writing Molecular, Complete Ionic, and Net Ionic Equations

Chemical equations are symbolic representations of chemical and physical changes. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations. Complete ionic and net ionic equations can be used to illustrate what is happening during precipitation reactions, neutralization reactions, gas evolving reactions, and single replacement reactions when these reactions occur in aqueous solutions.

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Adaptations to aid in student comprehension by Jackie MacDonald.

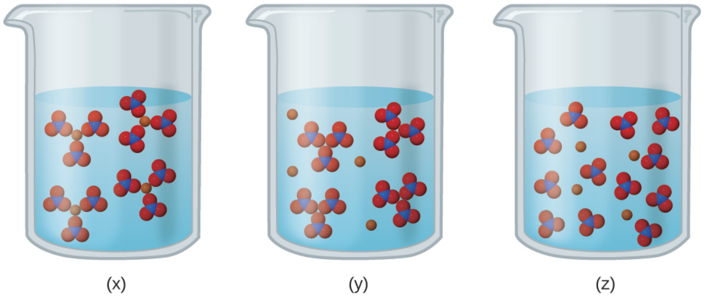
CHAPTER 15 - REVIEW

15.1 Salts

1. Explain how a salt is formed.
   Check answers: [1]
2. What salt will form when you combine hydrobromic acid and lithium hydroxide?
   Check answers: [2]
3. What salt will form when you combine sulfuric acid, H_2SO_4, and sodium hydroxide?
   Check answers: [3]

15.2 Electrolytes

1. Differentiate between strong and weak electrolytes.
   Check Answers: [4]
2. Explain why the ions Na^+ and Cl^- are strongly solvated in water but not in hexane, a solvent composed of nonpolar molecules. **Check Answer:** [5]
3. Explain why solutions of HBr in benzene (a nonpolar solvent) are nonconductive, while solutions in water (a polar solvent) are conductive.
4. Consider the solutions presented:
   a. Which of the following sketches, shown in the figure below, best represents the ions in a solution of $Fe(NO_3)_3(aq)$?



   b. Write a balanced chemical equation showing the products of the dissolution of $Fe(NO_3)_3$.
   Check Answer: [6]
5. Compare the processes that occur when methanol (CH_3OH), hydrogen chloride (HCl), and sodium

hydroxide (NaOH) dissolve in water. Write equations and prepare sketches showing the form in which each of these compounds is present in its respective solution.

6. What is the expected electrical conductivity of the following solutions?
   a. $NaOH(aq)$
   b. $HCl(aq)$
   c. $C_6H_{12}O_6(aq)$ (glucose)
   d. $NH_3(l)$

   Check Answer: [7]
7. Why are most *solid* ionic compounds electrically nonconductive, whereas aqueous solutions of ionic compounds are good conductors? Would you expect a *liquid* (molten) ionic compound to be electrically conductive or nonconductive? Explain.
8. Indicate the most important type of intermolecular attraction responsible for solvation in each of the following solutions:
   a. the solutions in Figure 14.2c
   b. methanol, CH_3OH, dissolved in ethanol, C_2H_5OH
   c. methane, CH_4, dissolved in benzene, C_6H_6
   d. the polar halocarbon CF_2Cl_2 dissolved in the polar halocarbon $CF_2ClCFCl_2$
   e. $O_2(l)$ in $N_2(l)$

   Check Answer: [8]

15.3 Precipitation Reactions

1. What are the general characteristics that help you recognize double replacement reactions?

   Check Answers: [9]
2. What are the general characteristics that help you recognize a precipitation reaction?

   Check Answers: [10]
3. Assuming that the following is a precipitation reaction, determine the products (and identify their phases, *aq* or *s*) and write the balanced chemical equation.

   $Zn(NO_3)_2 + NaOH \rightarrow ?$

   Check Answers: [11]
4. Assuming that the following is a precipitation reaction, determine the products (and identify their phases, *aq* or *s*) and write the balanced chemical equation.

   $MgCl_2 + NaOH \rightarrow$

   Check Answers: [12]
5. Use the solubility table to predict if the following double replacement reaction will occur and, if so, write a balanced chemical equation. $Pb(NO_3)_2 + KBr \rightarrow ?$

   Check Answers: [13]

6. Use the solubility table to predict if the following double replacement reaction will occur and, if so, write a balanced chemical equation.
   $KCl + Na_2CO_3 \rightarrow ?$
   Check Answers:[14]
7. Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?
   Check Answers: [15]

15.4 Net Ionic Equations

1. From the balanced molecular equations, write the complete ionic and net ionic equations for the following:
   (a) $K_2C_2O_4(aq) + Ba(OH)_2 \rightarrow 2KOH(aq) + BaC_2O_2(s)$
   (b) $Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2HNO_3(aq)$
   (c) $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$
   Check Answers: [16]
2. Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.
   (a) potassium sulfate and barium nitrate
   (b) lithium chloride and silver acetate
   (c) lead nitrate and ammonium carbonate
   Check Answers: [17]
3. From the balanced molecular equation, write the net ionic equations for the following reaction:
   $2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + H_2O(l)$
   Check Answers: [18]
4. From the balanced molecular equation, write the net ionic equations for the following reaction:
   $2AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$
   Check Answers: [19]

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- 15.3 Precipitation Reactions – Questions 1, 3, 5, 7 – adapted from "4.2 Classifying Chemical Reactions"In *CHEM 1114 – Introduction to Chemistry* by Shirley Wacowich-Sgarbi and Langara

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Notes

1. A salt is formed in a neutralization reaction of an acid and a base. Acids and bases always contain either a metal cation or a cation derived from ammonium (NH_4^+) and a nonmetal anion, the two can combine to form a salt.
2. the anion from the HBr is Br^-. The cation from LiOH is Li^+. The salt formed is LiBr, lithium bromide.
3. the anion from the H_2SO_4 is SO_4^{2-}. The cation from NaOH is Na^+. The salt formed is Na_2SO_4, sodium sulfate.
4. A strong electrolyte is a salt that fully ionizes (100%) in the aqueous solution and are great conductors of electricity. Whereas, with a weak electrolyte only a relatively small fraction of the dissolved substance undergoes the ion-producing process and therefore is a poor conductor of electricity.
5. Crystals of NaCl dissolve in water, a polar liquid with a very large dipole moment, and the individual ions become strongly solvated. Hexane is a nonpolar liquid with a dipole moment of zero and, therefore, does not significantly interact with the ions of the NaCl crystals.
6. (a) $Fe(NO_3)_3$ is a strong electrolyte, thus it should completely dissociate into Fe^{3+} and ($NO_3{}^-$) ions. Therefore, (z) best represents the solution. (b) $Fe(NO_3)_3(s) \longrightarrow Fe^{3+}(aq) + 3NO_3{}^-(aq)$
7. (a) high conductivity (solute is an ionic compound that will dissociate when dissolved); (b) high conductivity (solute is a strong acid and will ionize completely when dissolved); (c) nonconductive (solute is a covalent compound, neither acid nor base, unreactive towards water); (d) low conductivity (solute is a weak base and will partially ionize when dissolved)
8. (a) ion-dipole; (b) hydrogen bonds; (c) dispersion forces; (d) dipole-dipole attractions; (e) dispersion forces
9. A double replacement reaction occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products.
10. In a precipitation reactions, the reactants will be dissolved substances in aqueous solutions and will react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and a type of double displacement/replacement reaction.
11. $Zn(NO_3)_2(aq) + 2NaOH(aq) \rightarrow 2NaNO_3(aq) + Zn(OH)_2(s)$
12. $MgCl_2(aq) + 2NaOH(aq) \rightarrow 2NaCl(aq) + Mg(OH)_2(s)$
13. The reaction will occur since a precipitate will form. $Pb(NO_3)_2(aq) + 2KBr(aq) \rightarrow 2KNO_3(aq) + PbBr_2(s)$
14. No reaction occurs; both products are soluble in water. $2KCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + K_2CO_3(aq)$
15. sodium sulfate, $BaSO_4$
16. (a) complete ionic: $2K^+(aq) + C_2O_4{}^{2-}(aq) + Ba^{2+}(aq) + 2OH^-(aq) \rightarrow 2K^+(aq) + 2OH^-(aq) + BaC_2O_4(s)$ net ionic: $Ba^{2+}(aq) + C_2O_4{}^{2-}(aq) \rightarrow BaC_2O_4(s)$ (b) complete ionic: $Pb^{2+}(aq) + 2NO_3{}^-(aq) + 2H^+(aq) + SO_4{}^{2-}(aq) \rightarrow PbSO_4(s) + 2H^+(aq) + 2NO_3{}^-(aq)$ net ionic: $Pb^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow PbSO_4(s)$ (c) complete ionic: $CaCO_3(s) + 2H^+(aq) + SO_4{}^{2-}(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$ net ionic: $CaCO_3(s) + 2H^+(aq) + SO_4{}^{2-}(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

17. **(a)** The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction is$Ba^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow BaSO_4(s)$ **(b)** The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction is$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$ **(c)** The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction is$Pb^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow PbCO_3(s)$
18. $H+(aq) + OH^{-}(aq) \rightarrow H_2O(l)$
19. $2Ag^{+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

CHAPTER 16: ACIDS AND BASES

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- General characteristics and properties of acids and bases.
- Two models of acids and bases and the relationship between conjugate acid-base pairs.
- The autoionization of water.

- pH, pOH and the pH scale.
- How to calculate pH, pOH, and the acid and base concentration of various solutions.
- Neutralization reactions and how to do calculations involving strong acids and strong bases.
- Acid-Base titrations.
- The general characteristics of buffered solutions.

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- How to use your scientific calculator including the following functions (buttons): log, 10^x, scientific notation.
- Review double displacement reactions and net ionic equations.
- Understand concepts relating to ionization/dissociation of salts in solution.
- Polarity characteristics of water and its molecular equation.
- Performing molarity calculations of solutions to determine a solution's concentration.

Figure 16a Sinkhole Shown in Nature: Cenote Angelita is located in the state of Quintana Roo, in the Yucatan Peninsula of Mexico. Sinkholes in nature, such as this one, are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: work by Offthebeatonpath, CC BY-SA 3.0)

In our bodies, in our homes, and in our industrial society, acids and bases play key roles. Proteins, enzymes, blood, genetic material, and other components of living matter contain both acids and bases. We seem to like the sour taste of acids; we add them to soft drinks, salad dressings, and spices. Many foods, including citrus fruits and some vegetables, contain acids. Cleaners in our homes contain acids or bases. Acids and bases not only play important roles in the health/medical industry but also in the chemical industry. Huge quantities of sulfuric acid (H_2SO_4), ammonia (NH_3), urea (CH_4N_2O), and phosphoric acid (H_3PO_4) are released into the atmosphere, globally, every year. In Canada, the production of sulfuric acid is used by industry in the production of phosphate fertilizers, bleaching agents in pulp and paper manufacturing, and waste water processing in sewage treatment plants (Environment and Climate Change Canada, 2022, Sources and uses of sulfuric acid, para. 1). According to National Pollutant Release Inventory Overview by Environment and Climate Change Canada (2022),

> “the primary sources of sulfuric acid emissions are manufacturing, coal-fired power plants, petroleum and coal product refining and non-conventional oil extraction (including oil sands). These emissions are mostly to the air, with total air releases of 3485 tonnes in 2020. Electric power facilities, the manufacturing industry and pulp and paper plants discharged a combined 71 tonnes to water in 2020. A combined 16 tonnes of sulfuric acid was released to land from the mining and manufacturing industries. When burned, the sulfur content in fossil fuels is mostly converted into sulfur dioxide (SO_2),

> which can further oxidize into sulfur trioxide (SO_3) and then react with water to form sulfuric acid" (Releases of sulfuric acid section, para. 1).

For more information about sulfuric acid release in Canada or other pollution and waste management inventories visit the National Pollutant Release Inventory: tools and resources

Another factor that plays a crucial role in influencing chemical changes in our environment is acid rain. When precipitation from rain, snow, sleet, or hail falls to the earth, it collects acidic particles and gases dissolved in the atmosphere and turns the precipitation more acidic. Not only does acid deposition damage various ecosystems and physical structures, but also has negative health effects on its inhabitants, such as fish, wildlife, and human populations, (Environment And Climate Change Canada, 2018). To reference more about acid rain and its effects in Canada link visit Acid rain: causes and effects.

The history of the acid rain issues and its effects on the environment is a very intriguing phenomenon. **Watch Whatever happened to acid rain (5:39).**

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

Attribution & References

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References:

- Environment And Climate Change Canada. (2022, August 17). *National Pollutant Release Inventory overview: Sulphuric acid*. Canada.ca. Retrieved December 6, 2022.
- Environment And Climate Change Canada. (2018, June 27). *Acid rain: Causes and effects*. Canada.ca. Retrieved December 6, 2022.

16.1 ACIDS AND BASES

Learning Objectives

By the end of this section, you will be able to:

- Examine properties of acids and bases and provide examples of both
- Define a strong and a weak acid and base. Using a table for reference, recognize an acid or a base as strong or weak.
- Define an Arrhenius acid and Arrhenius base
- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Explain the Lewis model of acid-base chemistry

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible tasting coffee. Acids and bases are common substances found in many every day items, from fruit juices and soft drinks to soap. In this section, we'll explore the basic properties of acids and bases, and learn about the chemical nature of these important compounds.

Watch **The Strengths and Weaknesses of Acids and Bases (3min 47s).**

Acids: Properties and Examples

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid.

Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the colour of certain acid-base indicates. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colourless.
4. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.
5. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction (Chapter 8.3), as shown below:

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

Table 16.1a provides a partial list of some common acids and their uses.

Table 16.1a Common Acids and Their Uses

Compound Name and Chemical Formula	Common Name (if applicable)	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid is HCl	Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4	none	Used in car batteries, and in the manufacture of fertilizers.
nitric acid, HNO_3	none	Used in the manufacture of fertilizers, explosives and in extraction of gold.
acetic acid, $HC_2H_3O_2$	vinegar	Main ingredient in vinegar.
carbonic acid, H_2CO_3	responsible for the “fizz” in carbonated drinks	As an ingredient in carbonated drinks.
citric acid, $C_6H_8O_7$	none	Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

Later in this chapter, we will examine the chemistry behind what exactly makes an acid behave as an acid and what makes a base behave as a base. For now, take a look at the formulas given in the table 16.1a and take a guess as to what common feature characterizes an acid.

Figure 16.1a An Image of a solution containing Phenolphthalein Indicator: Phenolphthalein is often used as an indicator in acid–base titrations. It is colourless in acidic solutions and typically pink in basic solutions between a pH of 8.5-10. (credit: work by Ben Mills, PD)

Bases: Properties and Examples

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the HCl in the stomach and neutralize it, taking care of that unpleasant feeling. Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the colour of indicators. Litmus turns blue in the presence of a base, while phenolphthalein turns pink as shown in Figure 16.1a
4. Bases do not react with metals in the way that acids do but tend to react with fats and oils
5. Bases react with acids to produce a salt and water.

Warning!

Tasting chemicals and touching them are NOT good lab practices and should be avoided—in other words—don't do this at home.

Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. Antacids, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate.

Various common bases and corresponding uses are given in Table 16.1b.

Table 16.1b Common Bases and Corresponding Uses

Compound Name and Chemical Formula	Common Name (if applicable)	Uses
sodium hydroxide, NaOH	(lye or caustic soda)	Used in the manufacture of soaps and detergents, and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH	(lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$	(milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$	(slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide, $Al(OH)_3$		Used in water purification and as an ingredient in antacids.
ammonia, NH_3		Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

To learn more about commercially available acids and bases, see Appendix G.

Exercise 16.1a

Check Your Learning Exercise (Text Version)

Question 1 of Interactive:

For each of the following descriptions or properties, determine whether it is describing an acid or base:

1. Typically have a bitter taste
2. Solutions feel slippery
3. Turns litmus paper red
4. Turns litmus paper blue
5. Typically react with metals, producing hydrogen bubbles (gas)
6. Type of substance that aids in protein digestion in the stomach
7. The active ingredient of aspirin is this type of substance
8. Typically have a sour taste
9. Baking soda is classified as this
10. Citrus fruits are classified as this
11. Antacids are classified as this
12. Vinegar is classified as this

Question 2 of Interactive:

All of the follow are TRUE statements about bases EXCEPT

1. often an ingredient in cleaning solutions and feel slippery
2. when dissolved in water, have a bitter taste
3. Are electrolytes – conduct electricity
4. when metals are placed in a basic solution, they react, producing hydrogen bubbles

Question 3 of Interactive:

All of the follow are TRUE statements about ACIDS EXCEPT

1. acids are found in citrus fruits and provide the bitter taste
2. acids are found in citrus fruits and provide the sour taste
3. turns litmus paper red
4. Are electrolytes – conduct electricity

Question 4 of Interactive:

True or False? Both strong acids and bases can ionize in solution, which makes them electrolytes and can conduct an electrical current. However, only bases can dissolve metals, producing hydrogen gas.

Check Your Answer[1]

Source: "Exercise 16.1a" by Jackie MacDonald, licensed under CC BY-NC 4.0.

Strength of Acids and Bases

An acid or base's strength refers to its degree of ionization. We will explore the basics of acid/base strength below.

Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(*aq*). When HCl is dissolved in water (H_2O), it completely dissociates (100%) into $H^+(aq)$ and $Cl^-(aq)$ ions; all the HCl molecules become ions:

$$HCl \rightarrow H^+(aq) + Cl^-(aq)$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. Acetic Acid, $HC_2H_3O_2$, is an example of a weak acid (it does not dissociate completely in aqueous solution, only about 5%):

$$HC_2H_3O_2 \rightarrow H^+(aq) + C_2H_3O^{2-}(aq)$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as a reversible reaction:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O^{2-}(aq)$$

As it turns out, there are very few strong acids, which are given in Table 16.1c. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid.

Table 16.1c Strong Acids and Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
[Blank]	$Sr(OH)_2$
[Blank]	$Ba(OH)_2$

Strong and Weak Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table 16.1c); any base not listed is a weak base. All strong bases are compounds containing hydroxide, OH^-. Any other molecules classified as a base (using other mechanisms on defining bases), such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.

Molecular Definitions of Acids and Bases

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the colour of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. Three main classifications of acids and bases are predominantly used to explain acid base reactions:

1. Arrhenius acids and bases: Acids yield protons when dissolved in solution, while Arrhenius bases yields hydroxide ions.

2. Brønsted-Lowry acids and bases. Acids are proton donors, while Brønsted-Lowry bases are proton acceptors.
3. Lewis acids and bases: Acids are electron acceptors, while Lewis bases are electron donors.

Arrhenius Acids/Bases

The significance of hydrogen was reemphasized in 1884 when Carl Axel Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions, H_3O^+) and a base as a compound that dissolves in water to yield hydroxide anions (OH^-). In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did:

- An acid (**Arrhenius acid**) as a compound that dissolves in water to produce H^+ ions (in other words, yields hydronium ions, H_3O^+).
- A base (**Arrhenius base**) as a compound that dissolves in water to to yield hydroxide ions (OH^-).

This definition is not wrong; it is simply limited. The theory does not explain the weak base ammonia (NH_3), which in the presence of water, releases hydroxide ions into solution, but does not contain OH^- itself. The Arrhenius definition of acid and base is also limited to aqueous solutions.

Brønsted-Lowry Acids/Bases

Later in 1923 the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry proposed a more general definition of an acid or a base. Their definition centres on the proton, H^+. A proton is what remains when a normal hydrogen atom, ${}_{1}^{1}\mathrm{H}$, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$ HS^-, and HCO_3^- and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_5OH]^{2+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as NaOH and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$\mathrm{H^+ + OH^- \longrightarrow H_2O}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\begin{aligned}
\text{acid} &\leftrightharpoons \text{proton} + \text{conjugate base}\\
\text{HF} &\leftrightharpoons \text{H}^+ + \text{F}^-\\
\text{H}_2\text{SO}_4 &\leftrightharpoons \text{H}^+ + {\text{HSO}_4}^-\\
\text{H}_2\text{O} &\leftrightharpoons \text{H}^+ + \text{OH}^-\\
{\text{HSO}_4}^- &\leftrightharpoons \text{H}^+ + {\text{SO}_4}^{2-}\\
{\text{NH}_4}^+ &\leftrightharpoons \text{H}^+ + \text{NH}_3
\end{aligned}$$

Example 16.1a

Write the conjugate base for each of the following acids: (Hint! Remember an acid will donate a proton)

a. $HClO_4$
b. H_3PO_4
c. $CH_3NH_3^+$

Solution

a. $HClO_4$ is the acid; ClO_4^- is its conjugate base
b. H_3PO_4 is the acid; $H_2PO_4^-$ is its conjugate base
c. $CH_3NH_3^+$ is the acid; CH_3NH_2 is its conjugate base

Source: “Example 16.1a” by Jackie MacDonald is licensed under CC BY-NC 4.0.

Exercise 16.1b

Write the conjugate base for each of the following acids:

a. NH_2^-

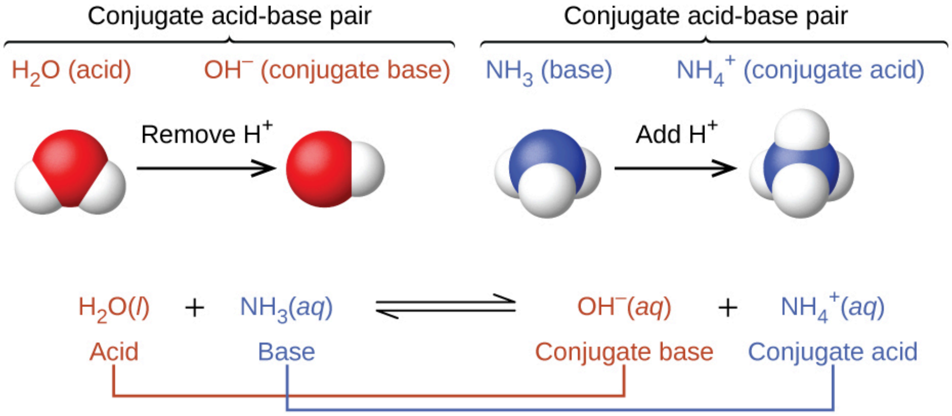
b. HBr
c. HSO_4^-

Check Your Answer[2] **Source: "Exercise 16.1b" by Jackie MacDonald is licensed under CC BY-NC 4.0.**

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\begin{array}{rcl} \text{base} + \text{proton} & \leftrightharpoons & \text{conjugate acid} \\ OH^- + H^+ & \leftrightharpoons & H_2O \\ H_2O + H^+ & \leftrightharpoons & H_3O^+ \\ NH_3 + H^+ & \leftrightharpoons & NH_4{}^+ \\ S^{2-} + H^+ & \leftrightharpoons & HS^- \\ CO_3{}^{2-} + H^+ & \leftrightharpoons & HCO_3{}^- \\ F^- + H^+ & \leftrightharpoons & HF \end{array}$$

In these two sets of equations, the behaviours of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the *transfer* of protons between acids and bases. Interestingly, water can act as an acid or base depending on what gets dissolved in it. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water (Figure 16.1b). A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+.



16.1b Acid-Base Reaction between Water and Ammonia showing Conjugate Acid-Base Pairs: A Brønsted-Lowry acid reacts with a base to form the conjugate base and acid, as shown with H_2O (acid) reacting with NH_3 (base) to form their respective conjugates. (credit: *Chemistry 2e (OpenStax)*, CC-BY-4.0).

The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:

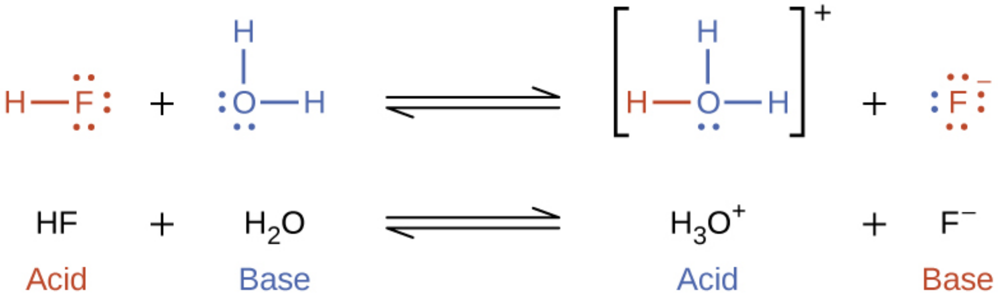


Figure 16.1c The Acid Ionization Reaction of an Acid (HF) with Water: The acid ionization reaction of an acid (HF) with water, resulting in formation of hydronium ions and the conjugate base of the acid. In this reaction, the water molecule functions as an base since it accepts a proton from the hydrofluoric acid (HF) molecule (functioning as a Brønsted-Lowry acid), yielding the conjugate acid of water, a hydronium ion (H_3O^+) and the conjugate base of hydrofluoric acid, F^-. (credit: *Chemistry 2e (OpenStax)*, CC-BY-4.0).

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:

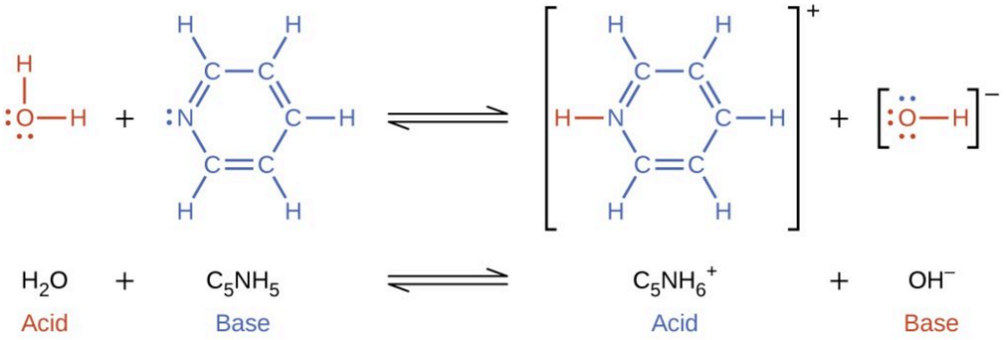


Figure 16.1d Pyridine Reacts with Water to Form the Pyridinium Ion and Hydronium Ion: In this reaction, the water molecule functions as an acid since it donates a proton to pyridine (functioning as a Brønsted-Lowry base), yielding the conjugate base of water, hydroxide ions (OH^-) and the conjugate acid of pyridine, pyridinium ions ($C_5NH_6^+$). (credit: *Chemistry 2e (OpenStax)*, CC-BY-4.0).

Notice that both these ionization reactions in Figure 16.1c and 16.1d are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic that will be covered in the equilibrium chapter.

Watch Conjugate Acids & Bases | Acids, Bases & Alkali's | Chemistry | FuseSchool (3min 45sec).

Example 16.1b

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. $NO^{2-} + H_2O \rightarrow HNO_2 + OH^-$
b. $HBr + H_2O \rightarrow H_3O^+ + Br^-$

Solution

a. H_2O is the Brønsted-Lowry acid and OH^- is its conjugate base; NO^{2-} is the Brønsted-Lowry base and HNO_2 is its conjugate acid.
b. HBr is the Brønsted-Lowry acid and Br^- is its conjugate base; H_2O is the Brønsted-Lowry base and H_3O^+ is its conjugate acid.

Exercise 16.1c

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. $HS^- + H_2O \rightarrow H_2S + OH^-$
b. $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$
c. $H_2PO_4^- + HCl \rightarrow H_3PO_4 + Cl^-$
d. $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$

Check Your Answer[3]

Exercise 16.1d

Check Your Learning Exercise (Text Version)

1. Correctly match each term with its correct definition:
   TERMS: (i) Brønsted-Lowry acid; (ii) Brønsted-Lowry base
   DEFINITIONS: (1) A compound that donates a proton to another compound; (2) a compound that accepts a proton
2. What is the conjugate acid in the following equation? $PO_4^{3-} + HNO_3 \rightarrow NO_3^{-} + HPO_4^{2-}$
3. What is the conjugate base in the following equation? $HCO_3^{-} + HCl \rightarrow H_2CO_3 + Cl^{-}$
4. Which of the following is the correct Brønsted-Lowry acid, conjugate base pair for the following reaction: $CH_3OH + H^{-} \rightarrow CH_3O^{-} + H_2$
   1. Brønsted-Lowry acid CH_3O^{-}, conjugate base CH_3OH
   2. Brønsted-Lowry acid CH_3OH, conjugate base CH_3O^{-}
   3. Brønsted-Lowry acid H^{-} , conjugate base H_2
   4. Brønsted-Lowry acid CH_3OH, conjugate base H^{-}

Check Your Answer[4]

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Lewis Acids and Bases

In 1923, G. N. Lewis proposed a generalized definition of acid-base behaviour in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

A **coordinate covalent bond** (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown in Figure 16.1e.

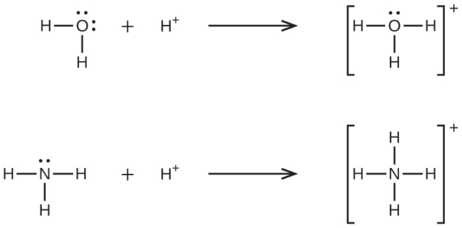

Figure 16.1e Illustrating Coordinate Covalent Bonds: Two chemical equations are shown to illustrate Lewis acids and base reactions: the formation of a hydronium ion and an ammonium ion. (credit: *Chemistry (OpenStax)* , CC BY 4.0)

A **Lewis acid** is any species (molecule or ion) that can accept a pair of electrons, and a **Lewis base** is any species (molecule or ion) that can donate a pair of electrons.

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid. A **Lewis acid-base adduct**, a compound that contains a coordinate covalent bond between the Lewis acid and the Lewis base, is formed. The following equations illustrate the general application of the Lewis concept.

The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs as demonstrated in Figure 16.1f:

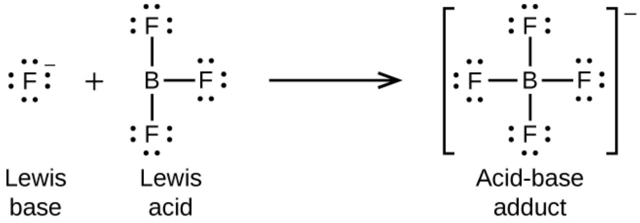

Figure 16.1f Lewis Acid-Base Reaction Involving Boron Trifluoride: The Lewis base, a fluorine ion, reacts with a Lewis acid, boron trifluoride, to produce boron tetrafluoride, which is an acid-base adduct. (credit: *Chemistry (OpenStax)* , CC BY 4.0).

Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions as shown in Figure 16.1g.

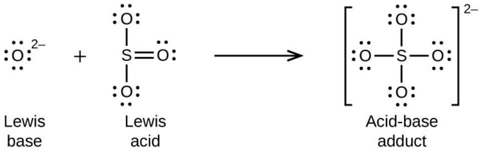

Figure 16.1g Lewis Acid-Base Reaction Involving Nonmetal Oxides: The Lewis base, an oxygen ion, reacts with a Lewis acid, sulfur trioxide, to produce a sulphate ion, which is an acid-base adduct. (credit: *Chemistry (OpenStax)* , CC BY 4.0)

Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid (Figure 16.1h):

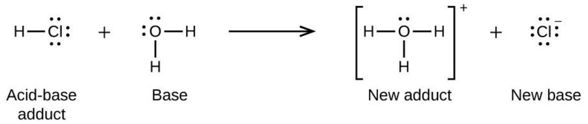

Figure 16.1h Lewis Acid-Base Displacement Reaction: In this reaction, HCl is an acid-base adduct that reactants with water, which is behaving as a base, to form a new adduct (hydronium ion) and a new base (chloride ion) (credit: *Chemistry (OpenStax)*, CC BY 4.0)

The displacement reaction in Figure 16.1h shows how the reaction of a Brønsted-Lowry acid with a base fits into the Lewis concept. A Brønsted-Lowry acid such as HCl is an acid-base adduct according to the Lewis concept, and proton transfer occurs because a more stable acid-base adduct is formed. Thus, although the definitions of acids and bases in the two theories are quite different, the theories overlap considerably.

Amphiprotic / Amphoteric Species

As illustrated in the previous paragraphs water can behave as an acid or a base. Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be **amphiprotic**. Another term used to describe such species is **amphoteric**, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO_3{}^-(aq) + H_2O(l) \leftrightharpoons CO_3{}^{2-}(aq) + H_3O^+(aq)$$

$$HCO_3{}^-(aq) + H_2O(l) \leftrightharpoons H_2CO_3(aq) + OH^-(aq)$$

Example 16.1c

Representing the Acid-Base Behaviour of an Amphoteric Substance

Write separate equations representing the reaction of $HSO_3{}^-$.

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3{}^-(aq) + OH^-(aq) \leftrightharpoons SO_3{}^{2-}(aq) + H_2O(l)$
b. $HSO_3{}^-(aq) + HI(aq) \leftrightharpoons H_2SO_3(aq) + I^-(aq)$

Exercise 16.1e

Write separate equations representing the reaction of H_2PO_4.

a. as a base with HBr
b. as an acid with OH^-

Check Your Answer[5]

Links to Interactive Learning Tools

Explore Acid-Base Properties from the Physics Classroom.

Explore Bronsted-Lowry Acid and Base Model from the Physics Classroom.

Attribution & References

Except where otherwise noted, this section is adapted by Jackie MacDonald from "14.2: Acids- Properties and Examples", "14.3: Bases- Properties and Examples", and "14.7: Strong and Weak Acids and Bases" In *Map: Introductory Chemistry (Tro)* by Marisa Alviar-Agnew & Henry Agnew, Shared under CK-12 license. / Content streamlined and remixed for student comprehension.

- "Molecular Definitions of Acids and Bases" and "Amphiprotic / Amphoteric Species" sections are adapted from “14.1 Brønsted-Lowry Acids and Bases” and “15.2 Lewis Acids and Bases” In *General Chemistry 1 & 2* by Rice University, licensed under CC BY 4.0 International License, Except where otherwise noted. / Wording modifications by Jackie MacDonald.

Notes

1. Question 1:
    1. base;
    2. base;
    3. acid;
    4. base;
    5. acid;
    6. acid;
    7. acid;
    8. acid;
    9. base;
    10. acid;
    11. base;
    12. acid;

    Question 2: (4) when metals are placed in a basic solution, they react, producing hydrogen bubbles; Question 3: acids are found in citrus fruits and provide the bitter taste; Question 4: FALSE
2.
    1. when NH_2^- is the acid; NH_3 is its conjugate base;
    2. when HBr the acid; Br^- is its conjugate base;
    3. When HSO_4^- is the acid; SO_4^{2-} is the base.
3.
    a. H_2O is the Brønsted-Lowry acid and OH^- is its conjugate base; HS^- is the Brønsted-Lowry base and H_2S is its conjugate acid;
    b. $H_2PO_4^-$ is the Brønsted-Lowry acid and HPO_4^{2-} is its conjugate base; OH^- is the Brønsted-Lowry base and H_2O is its conjugate acid;
    c. HCl is the Brønsted-Lowry acid and Cl^- is its conjugate base; $H_2PO_4^-$ is the Brønsted-Lowry base and H_3PO_4 is its conjugate acid;
    d. $[Al(H_2O)_6]^{3+}$ is the Brønsted-Lowry acid and $[Al(H_2O)_5(OH)]^{2+}$ is its conjugate base; $[Fe(H_2O)_5(OH)]^{2+}$ is the Brønsted-Lowry base and $[Fe(H_2O)_6]^{3+}$ is its conjugate acid.
4.
    1. (i) Brønsted-Lowry acid = (1) A compound that donates a proton to another compound; (ii) Brønsted-Lowry base = (2) a compound that accepts a proton
    2. HPO_4^{2-}
    3. Cl^-
    4. 2. Brønsted-Lowry acid CH_3OH, conjugate base CH_3O^-
5.
    a. $H_2PO_4{}^-(aq) + HBr(aq) \leftrightharpoons H_3PO_4(aq) + Br^-(aq)$;
    b. $H_2PO_4{}^-(aq) + OH^-(aq) \leftrightharpoons HPO_4{}^{2-}(aq) + H_2O(l)$

16.2 REACTIONS OF ACIDS AND BASES

Learning Objectives

By the end of this section, you will be able to:

- Summarize general reactions of acids and bases

In this section, the more common types of acid-base reactions that take place in aqueous solutions will be summarized. In continuation with the context learned earlier in this chapter, a strong acid is a substance that will dissolve in water to yield hydronium ions, H_3O^+. Whereas, a strong base is a substance that will dissolve in water to yield hydroxide ions, OH^-. We will learn other definitions of acids and bases in the following sections. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion. For example, NaOH and $Ca(OH)_2$. When these compounds dissolve in water, hydroxide ions are released directly into the solution. These ions are responsible for the characteristic behaviour of acids and bases in aqueous solution.

Neutralization Reactions

The reaction between an acid and a base is called an acid-base reaction or a **neutralization reaction**. Later in this chapter, a section is dedicated to discussing neutralization reactions and introducing calculations relating to neutralization reactions. However, a brief introduction into this type of reaction is provided. In reactions where the acid is a hydrogen-ion-containing compound and the base is a hydroxide-ion-containing compound, the two react chemically to form water and a salt. The general form for a neutralization reaction is

$$\text{acid} + \text{base} \rightarrow \text{water} + \text{salt}$$

where the term salt is used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base, as outlined in chapter 15. In chemistry, the word salt refers to more than just table salt. For example, the balanced chemical equation for the reaction between HCl(*aq*) and KOH(*aq*) is

$$HCl(aq) + KOH(aq) \rightarrow H_2O(l) + KCl(aq)$$

where in this instance, the salt is soluble potassium chloride, KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between $HCl(aq)$ and $Mg(OH)_2(aq)$, additional molecules of HCl and H_2O are required to balance the chemical equation:

$$2HCl(aq) + Mg(OH)_2(aq) \rightarrow 2H_2O(l) + MgCl_2(aq)$$

Here, the soluble salt is $MgCl_2$. (This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid.)

There are acid-base reactions that do not follow the "general acid-base" equation given above. For example, the balanced chemical equation for the reaction between $HCl(aq)$ and $NH_3(aq)$ is

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between $HCl(aq)$ and $Fe(OH)_3(s)$ still proceeds according to the equation

$$3\ HCl(aq) + Fe(OH)_3(s) \rightarrow 3H_2O(l) + FeCl_3(aq)$$

even though $Fe(OH)_3$ is not soluble. When one realizes that $Fe(OH)_3(s)$ is a component of rust, this explains why some cleaning solutions for rust stains contain acids — the neutralization reaction produces products that are soluble and wash away. Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!

Gas-Forming Acid-Base Reactions

A driving force for certain acid-base reactions is the formation of a gas. Common gases formed are hydrogen (H_2), oxygen (O_2), and carbon dioxide (CO_2).

Acid Reactions with Carbonates

Many acids react with carbonates to produce a salt, carbon dioxide gas and water.

$$\text{acid} + \text{carbonate} \rightarrow \text{salt} + CO_2(g) + H_2O(l)$$

Consider the following reaction between hydrochloric acid and sodium carbonate (which is considered a base):

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow H_2CO_3(aq) + 2NaCl(aq) \rightarrow CO_2(g) + H_2O(l) + 2NaCl(aq)$$

The above example can be viewed as an acid-base reaction followed by a decomposition. The driving force in this case is the gas formation. The decomposition of H_2CO_3 into CO_2 and H_2O is a very common reaction. Both sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) mixed with acid result in a gas-forming acid-base reaction.

$$HCl(aq) + NaHCO_3(aq) \rightarrow H_2CO_3(aq) + NaCl(aq) \rightarrow CO_2(g) + H_2O(l) + NaCl(aq)$$

More Reactions Involving Acids and Bases

There are many common reactions of acids chemically combining with carbonate, to form a salt and carbonic acid as demonstrated above. Due to the chemical disposition of carbonic acid as weak acid, it readily decomposes to water and carbon dioxide gas. The final products of chemical reactions are shown for examples 1 through 3 below, but remember that the formation of carbonic acid occurs as an intermediate step before decomposing to the final products.

- Example 1: Nitric acid reacts with sodium carbonate to form sodium nitrate, carbon dioxide, and water.

$$2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + CO_2(g) + H_2O(l)$$

- Example 2: Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide, and water:

$$2HCl(aq) + CaCO_3(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

- Example 3: Sulfuric acid reacts with calcium carbonate to form calcium sulfate, carbon dioxide, and water:

$$H_2SO_4(aq) + CaCO_3(aq) \rightarrow CaSO_4(aq) + CO_2(_g) + H_2O(l)$$

Watch **Acid + Metal Carbonate | Acids, Bases & Alkalis | Chemistry | FuseSchool (3min 0s)**.

Acid Reactions with Metals

The oxidation of metals in acidic solutions is another chemical process that generates a gas. This reaction will yield a metal salt and hydrogen gas and has the general formula

acid + metal → hydrogen + salt

Consider the following single displacement reaction between hydrochloric acid and solid zinc metal.

$$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$

Here, hydrochloric acid reacts with zinc to produce an aqueous metal salt and hydrogen gas bubbles.

Base Reactions with Metals

Some bases can also react with metals to form a gaseous product. For instance, strong bases, such as sodium hydroxide and potassium hydroxide, react with amphoteric metals to produce hydrogen gas and a salt:

Base + metal + water → hydrogen + salt

Consider the following example of sodium hydroxide reacting with Zinc in water to form sodium aluminate and hydrogen gas.

$$2NaOH(aq) + Zn(s) \rightarrow Na_2Zn(OH)_4(aq) + H_2(g)$$

Reactions with Metal Oxides

The oxides of metals are basic and when a metal oxide reacts with an acid, it forms a salt with water.

$$\text{acid} + \text{metal oxide} \rightarrow \text{salt} + H_2O(l)$$

An example of this type of reaction is mixing a small amount of the black, insoluble salt, copper(II) oxide, with dilute sulfuric acid. Upon mixing of the reactants, the colour of the solution becomes blue and the copper oxide dissolves. The blue colour of the solution indicates the formation of the soluble salt, copper(II) sulfate and water.

This chemical reaction can be written as the following:

$$CuO(s) + H_2SO_4\,(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$

Figure 16.2a Crystal of Copper(II) Sulfate: Sample of the collection of artificial minerals from the Natural History Museum Lille. This blue crystal of copper(II) sulfate is of industrial origin, created by slow crystallization from a saturated solution. (credit: work by Lamiot, CC BY-SA 4.0).

Source: Except where otherwise noted, "More Reactions Involving Acids & Bases" is created by Jackie MacDonald, CC BY-NC-SA 4.0

Food and Drink: Acids in Foods

Many foods and beverages contain acids. Acids impart a sour note to the taste of foods, which may add some pleasantness to the food. For example, orange juice contains citric acid, $H_3C_6H_5O_7$. Note how this formula shows hydrogen atoms in two places; the first hydrogen atoms written are the hydrogen atoms that can form H^+ ions, while the second hydrogen atoms written are part of the citrate ion, $C_6H_5O_7^{3-}$. Lemons and limes contain much more citric acid—about 60 times as much—which accounts for these citrus fruits being more sour than most oranges. Vinegar is essentially a ~5% solution of acetic acid ($HC_2H_3O_2$) in water. Apples contain malic acid ($H_2C_4H_4O_5$; the name *malic acid* comes from the apple's botanical genus name, *malus*), while lactic acid ($HC_3H_5O_3$) is found in wine and sour milk products, such as yogurt and some cottage cheeses.

Table 16.2a "Various Acids Found in Food and Beverages" lists some acids found in foods, either naturally or as an additive. Frequently, the salts of acid anions are used as additives, such as monosodium glutamate (MSG), which is the sodium salt derived from glutamic acid. As you read the list, you should come to the inescapable conclusion that it is impossible to avoid acids in food and beverages.

Table 16.2a Various Acids Found in Food and Beverages

Acid Name	Acid Formula	Use and Appearance
acetic acid	$HC_2H_3O_2$	flavouring; found in vinegar
adipic acid	$H_2C_6H_8O_4$	flavouring; found in processed foods and some antacids
alginic acid	various	thickener; found in drinks, ice cream, and weight loss products
ascorbic acid	$HC_6H_7O_6$	antioxidant, also known as vitamin C; found in fruits and vegetables
benzoic acid	$HC_6H_5CO_2$	preservative; found in processed foods
citric acid	$H_3C_6H_5O_7$	flavouring; found in citrus fruits
dehydroacetic acid	$HC_8H_7O_4$	preservative, especially for strawberries and squash
erythrobic acid	$HC_6H_7O_6$	antioxidant; found in processed foods
fatty acids	various	thickener and emulsifier; found in processed foods
fumaric acid	$H_2C_4H_2O_4$	flavouring; acid reactant in some baking powders
glutamic acid	$H_2C_5H_7NO_4$	flavouring; found in processed foods and in tomatoes, some cheeses, and soy products
lactic acid	$HC_3H_5O_3$	flavouring; found in wine, yogurt, cottage cheese, and other sour milk products
malic acid	$H_2C_4H_4O_5$	flavouring; found in apples and unripe fruit
phosphoric acid	H_3PO_4	flavouring; found in some colas
propionic acid	$HC_3H_5O_2$	preservative; found in baked goods
sorbic acid	$HC_6H_7O_2$	preservative; found in processed foods
stearic acid	$HC_{18}H_{35}O_2$	anticaking agent; found in hard candies
succinic acid	$H_2C_4H_4O_4$	flavouring; found in wine and beer
tartaric acid	$H_2C_4H_4O_6$	flavouring; found in grapes, bananas, and tamarinds

Attribution & References

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16.3 IONIZATION OF WATER

Learning Objectives

By the end of this section, you will be able to:

- Describe the autoionization of water
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations

To begin this chapter, **Watch** **How Polarity makes Water Behave Strangely (3min 51s).**

Earlier in this chapter, the concept of amphoteric species, such as water, was introduced. Because of its highly polar structures, water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions (Figure 16.3a).

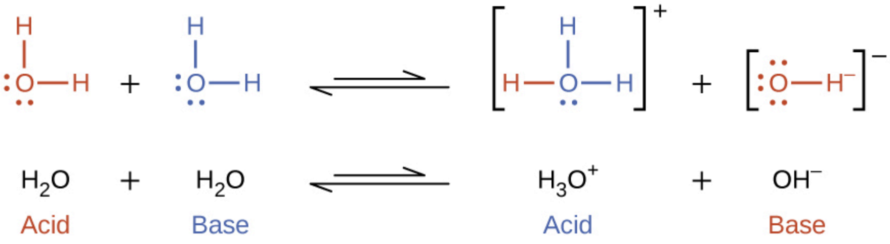

Figure 16.3a Autoionization of Water: Water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**.

To visualize this process in a video simulation, **watch** **Autoionization in Liquid Water (3 min 23s).**

Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The relationship between products and reactants of any reaction at equilibrium can be expressed by its equilibrium constant, K. The equilibrium constant for the ionization of water is called the **ion-product constant for water (K_w)**:

$$\mathrm{H_2O}(l) + \mathrm{H_2O}(l) \leftrightharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}]$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 16.3a

Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$. At 25 °C:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = [\mathrm{H_3O^+}]^2 = [\mathrm{OH^-}]^2 = 1.0 \times 10^{-14}$$

So:

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal 1.0×10^{-7} *M*.

Therefore, at 25 °C, K_w has a value of 1.0×10^{-14}.

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$$

The degree of autoionization of water and hence the value of Kw changes with temperature, so the equation

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$$

is accurate only at room temperature. If a temperature is not given in a question, assume room temperature.

Exercise 16.3a

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Check Your Answer[1]

Calculating Hydronium and Hydroxide Concentrations in Solutions using K_w

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Pure water is considered a **neutral solution**. Adding an acid or base to water will not change the position of the equilibrium.

Ion Concentrations in Water

At 25°C,

- In a neutral solution, the $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M
- In an acidic solution, the concentration of $H_3O^+(aq)$ is greater than 1.0×10^{-7} M, and thus, its $[OH^-]$ will be less than 1.0×10^{-7} M
    - In an acidic solution, the $[H_3O^+] > [OH^-]$
- For basic solutions, the concentration of $OH^-(aq)$ is greater than 1.0×10^{-7} M, and thus, its $[H_3O^+]$ will be less than 1.0×10^{-7} M
    - In a basic solution, the $[OH^-] > [H_3O^+]$

However, remember the product of the two concentrations $[H_3O^+][OH^-]$ is always equal to 1.0×10^{-14} M, no matter whether the aqueous solution is an acid, a base, or neutral:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\ M$$

Consequently, if you know $[H_3O^+]$ for a solution, you can use the K_w formula to calculate the $[OH^-]$.

Alternatively, if you know [OH^-], you can calculate [H_3O^+]. This means in any given acid/base solution the two concentrations are inversely related: As one concentration increases, the other must decrease, so their product always equals the value of K_W.

Source: "Ion Concentrations in Water" by Jackie MacDonald, CC BY-NC-SA 4.0

Example 16.3b demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations. At 25°C, $K_\text{w} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$.

Example 16.3b

The Inverse Proportionality of [H_3O^+] and [OH^-]

A solution of carbon dioxide in water has a hydronium ion concentration of 2.0×10^{-6} *M*. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$$

$$K_\text{w} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_W expression yields that [OH^-] is directly proportional to the inverse of [H_3O^+]:

$$[\text{OH}^-] = \frac{K_\text{w}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to 5.0×10^{-9} *M* as the hydrogen ion concentration increases to 2.0×10^{-6} *M*. This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the [OH^-] is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_\text{w} = [\text{H}_3\text{O}^+][\text{OH}^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 16.3b

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 *M* at 25 °C?

Check Your Answer[2]

Exercise 16.3c

Practice using the following PhET simulation: pH Scale

Example 16.3c

For the following solutions, determine whether the solution is acidic, basic or neutral.

1. A solution that has a $[H_3O^+] = 3.5 \times 10^{-3}\ M$
2. A solution that has a $[OH^-] = 1.0 \times 10^{-7}\ M$
3. A solution that has a $[H_3O^+] = 3.5 \times 10^{-12}\ M$

Solution

1. Since the solution's $[H_3O^+]$ of $3.5 \times 10^{-3}\ M$ is greater than $1.0 \times 10^{-7} M$, the solution is acidic.
2. Since the solution's $[OH^-]$ of $1.0 \times 10^{-7} M$ is equal to $1.0 \times 10^{-7} M$, the solution is neutral.
3. Since the solution's $[H_3O^+]$ of $3.5 \times 10^{-12}\ M$ is less than $1.0 \times 10^{-7} M$, its $[OH^-]$ will be greater $1.0 \times 10^{-7} M$, which indicates the solution is basic.

Activity Source: "Example 16.3c" created by Jackie MacDonald is licensed under CC BY-NC-SA 4.0.

Exercise 16.3d

Check Your Learning Exercise (Text Version)
For the following solutions, determine whether the solution is acidic, basic or neutral.

1. A solution that has a $[H_3O^+] = 2.5 \times 10^{-12}$ *M*
2. A solution that has a $[H_3O^+] = 9.0 \times 10^{-4}$ *M*
3. A solution that has a $[H_3O^+] = 1.0 \times 10^{-7}$ *M*
4. A solution that has a $[OH^-] = 1.0 \times 10^{-9}$ *M*
5. A solution that has a $[OH^-] = 1.0 \times 10^{-7}$ *M*
6. A solution that has a $[OH^-] = 4.8 \times 10^{-2}$ *M*

Check Your Answer[3]

Source: "Exercise 16.3d" by Jackie MacDonald, licensed under CC BY NC SA 4.0.

Key Equations

- $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)

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Notes

1. $[H_3O^+] = [OH^-] = 4.9 \times 10^{-7} M$
2. $[H_3O^+] = 1 \times 10^{-11} M$
3. (1) Basic; (2) Acidic; (3) Neutral; (4) Acidic; (5) Neutral; (6) Basic

16.4 INTRODUCTION TO PH AND POH

Learning Objectives

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviours of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions. To assist with informing users of a substance's acidity or basicity (alkalinity), one can calculate the pH of the substance and reference it on the pH scale. For a brief introduction into the pH scale and how it is used, **Watch The pH Scale Explained (5min 54s).**

Introduction to the pH Scale

The **pH scale** is a scale of acidity ranging 0 to 14 (but not always). It indicates how acidic or basic a solution is. You can use **pH** to make a quick determination whether a given aqueous solution is acidic, basic, or neutral. Since the pH of a substance is dependent on hydronium ion concentration, $[H_3O^+]$, the following conclusions (at standard temperature of 25 °C) can be inferred:

- If pH < 7, then the solution is acidic.

- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

Most substances have a pH in the range of 0 to 14, although *extremely* acidic or alkaline substances may have pH < 0, or pH > 14, respectively.

Source: "pH" by Simple English Wikipedia, licensed under CC BY-SA 3.0.

Exercise 16.4a

Check Your Learning Exercise (Text Version)
Label each solution as acidic, basic, or neutral based only on the given pH value:

1. Household bleach, pH = 12.6
2. Lime Juice, pH = 2.3
3. Milk of Magnesia, pH = 10.5
4. Pure Water, pH = 7
5. Vinegar, pH = 2.5
6. Baking soda, pH = 8.5

Check Your Answer[1]

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Formulas for Calculating pH, pOH, [H_3O^+] and [OH^-]

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH**:

$$\text{pOH} = -\log[\text{OH}^-]$$

or

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\text{w} = [H_3O^+][OH^-]$$
$$-\log K_\text{w} = -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + -\log[OH^-]$$
$$pK_\text{w} = \text{pH} + \text{pOH}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \text{pH} + \text{pOH}$$

As was shown in Example 16.3a in Chapter 16.3 Ionization of Water, Brønsted-Lowry Acids and Bases, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} M at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00$$
$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} M and hydroxide ion molarities less than 1.0×10^{-7} M (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than 1.0×10^{-7} M and hydroxide ion molarities greater than 1.0×10^{-7} M (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} M, which corresponds to pH and pOH values of:

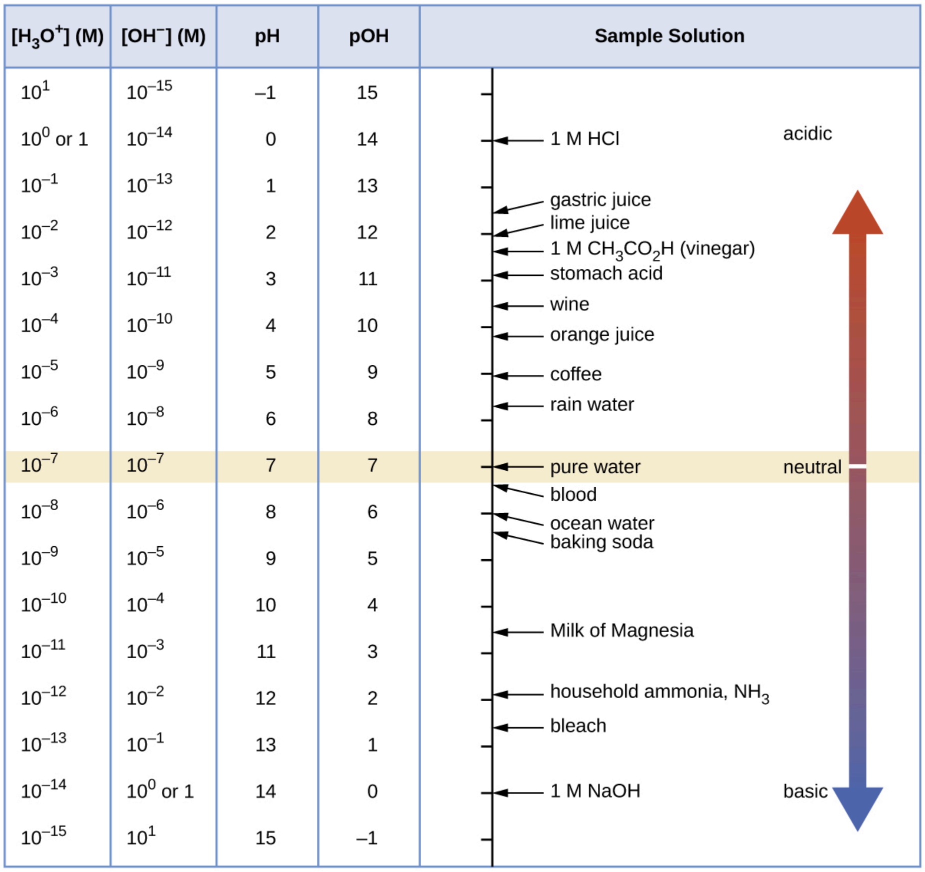
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.9 \times 10^{-7}) = 6.31$$
$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 16.4a).

Table 16.4a Summarizing pH Properties for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure 16.4a shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.



$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH
10^{1}	10^{-15}	–1	15
10^{0} or 1	10^{-14}	0	14
10^{-1}	10^{-13}	1	13
10^{-2}	10^{-12}	2	12
10^{-3}	10^{-11}	3	11
10^{-4}	10^{-10}	4	10
10^{-5}	10^{-9}	5	9
10^{-6}	10^{-8}	6	8
10^{-7}	10^{-7}	7	7
10^{-8}	10^{-6}	8	6
10^{-9}	10^{-5}	9	5
10^{-10}	10^{-4}	10	4
10^{-11}	10^{-3}	11	3
10^{-12}	10^{-2}	12	2
10^{-13}	10^{-1}	13	1
10^{-14}	10^{0} or 1	14	0
10^{-15}	10^{1}	15	–1

Figure 16.4a Relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Determining pH and pOH from its Reciprocal pH/pOH Value

pOH scale is fairly similar to pH, except instead of measuring the hydrogen ion concentration in moles per litre, it measures the hydroxide ion concentration in moles per litre. As shown earlier in this section (during standard temperature conditions), pH and pOH must add up to 14:

$$14.00 = \text{pH} + \text{pOH}$$

So if you are given pH, you can determine pOH by rearranging the formula:

$$\text{pOH} = 14 - \text{pH}$$

Alternatively, if you are given pOH, you can determine pH by rearranging the formula:

$$\text{pH} = 14 - \text{pOH}$$

Example 16.4a

A cleaning solution has a pOH of 2.5. Calculate the pH of this solution and determine whether this solution is acidic, basic, or neutral.

Solution

Given information

pOH = 2.5

To find the pH, use the formula

pH = 14 – pOH

Solve:

pH = 14 – 2.5

pH = 11.5; this cleaning solution is basic since its pH is greater than 7.

Exercise 16.4b

Exercise 16.4b Part 1:

For each solution listed below, calculate its pOH and determine whether this solution is acidic, basic, or neutral.

a. Solution that has a pH = 9.25
b. Solution that has a pH = 3.8

Exercise 16.4b Part 2:

For each solution listed below, calculate its pH and determine whether this solution is acidic, basic, or neutral.

a. Solution that has a pOH = 5.65
b. Solution that has a pOH = 13.1

Check Your Answer[2]

Essentially, the scale for pOH is the reverse of the pH scale.

Source: "Determining pH and pOH from its Reciprocal pH/pOH Value" by Jackie MacDonald, CC-BY-NC-SA 4.0

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 16.4c).

(a) (b)

Figure 16.4b (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of 1000 dollars. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit a: work by Datamax, PD; credit b: modification of work by Laurence Livermore, CC BY 2.0)

The pH of a solution may also be visually estimated using coloured indicators (Figure 16.4d).

(a) (b)

Figure 16.4c (a) A universal indicator assumes a different colour in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH3CO2H (pH = 3), and NH4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, C6H5NH2 (pH = 9), NH3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colours in solutions of differing pH values. (credit: modification of work by Sahar Atwa in *Chemistry (OpenStax)*, CC BY 4.0).

Calculating pH when given Hydronium Concentration

When you are given a solution's hydronium concentration, its pH can be calculated using the formula:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$$

Example 16.4b

Calculation of pH from [H_3O^+]

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} *M*?

Solution

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

(The use of logarithms is explained in Appendix B – The Use of Logarithms and Exponential Numbers Section).

Recall that, as we have done here, when taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.). To review significant figures for logarithm calculations, **Watch Significant Figures and Logarithms (2min 0s).**

Exercise 16.4c

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\text{CO}_2(aq) + \text{H}_2\text{O}(l) \leftrightharpoons \text{H}_2\text{CO}_3(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of 2.0×10^{-6} *M*, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Check Your Answer[3]

Calculating Hydronium Concentration when given the pH

When you are given a solution's pH, its hydronium concentration can be calculated using the formula:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}$$

Example 16.4c

Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood that has a pH of 7.3 (slightly alkaline).

Solution

Use the formula:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}$$

Solve given that the pH = 7.3

$[H_3O^+] = 10^{-7.3}$

$[H_3O^+] = 5 \times 10^{-8}$ *M*

Therefore, the hydronium ion concentration of blood with a pH of 7.3 is 5×10^{-8} *M*

Source: "Example 16.4c" by Jackie MacDonald, CC-BY-NC-SA 4.0

Exercise 16.4d

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Check Your Answer[4]

Source: "Exercise 16.4d" by Jackie MacDonald, CC-BY-NC-SA 4.0

Calculating pOH when given Hydroxide Concentration

When you are given a solution's hydronium concentration, its pH can be calculated using the formula:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

Example 16.4d

What are the pOH and the pH of a 0.0125 *M* solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-]$ = 0.0125 *M*:

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] \\ &= -\log(0.0125) \\ &= -(-1.903) \\ &= 1.903 \end{aligned}$$

The pH can be found from the pOH:

$$\begin{aligned} \text{pH} + \ \text{pOH} &= 14.00 \\ \text{pH} &= 14.00 \ - \ \text{pOH} \\ &= 14.00 \ - \ 1.903 \\ &= 12.10 \end{aligned}$$

Exercise 16.4e

The hydroxide concentration of a sodium hydroxide solution is 0.091 *M*. Determine the pOH and pH of the solution.

Check Your Answer[5]

Calculating Hydroxide Concentration when given the pOH

When you are given a solution's hydronium concentration, its pH can be calculated using the formula:

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}}$$

Example 16.4e

Calculation of [OH⁻]

The pOH of house hold bleach is 1.45. What is the $[OH^-]$ of this solution?

Solution

Use the formula $[OH^-] = 10^{-pOH}$ to determine the hydroxide concentration of the bleach solution.

$[OH^-] = 10^{-pOH}$

$[OH^-] = 10^{-1.45}$

$[OH^-] = 0.035$ *M* or 3.5×10^{-2} *M*

Source: "Example 16.4e" by Jackie MacDonald, CC-BY-NC-SA 4.0

Exercise 16.4f

The pOH of toilet a bowl cleaner is measured to be 12.35. What is the [OH^-] of this solution? Is this solution acidic or basic?

Check Your Answer[6] **Source: "Exercise 16.5f" by Jackie MacDonald, CC-BY-NC-SA 4.0**

Acid/Base Calculations involving Two Steps

Figure 16.4b below shows all of the calculation interrelationships between [H_3O^+], [OH^-], pH, and pOH. The flow chart can be referenced to support students in determining which formula(s) need to be used to solve a given problem.

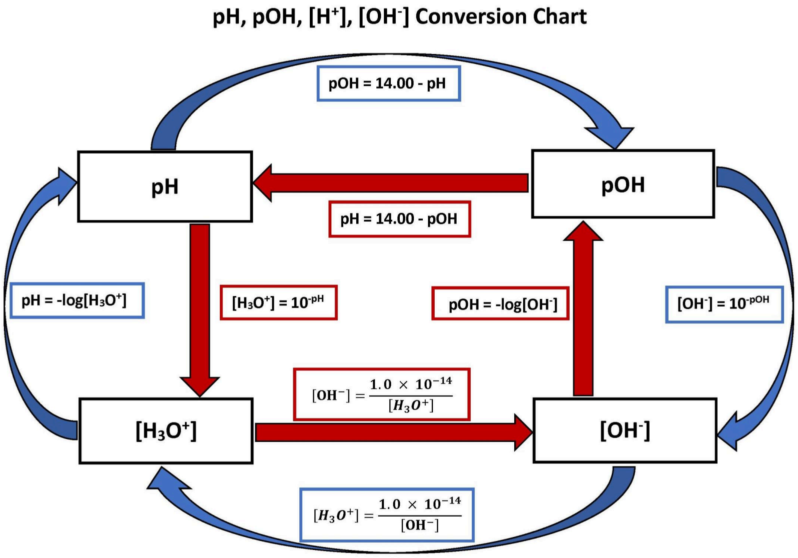


Figure 16.4d Calculation Relationships between Hydrogen Ion Concentration, Hydroxide Concentration, pH and pOH: Use the flow chart to determine which formula(s) to use to answer an acid/base calculation. To begin, locate the unit of the given information on the diagram that was provided in the question. Next, locate the unit of the answer you are asked to calculate. Use the formula(s) to solve the question that is associated with the arrow(s) pointing in the direction of the unit you are trying to calculate. It may be a one step or two step problem. (credit: Figure 16.4b by Jackie MacDonald, CC-BY-NC-SA 4.0).

Example 16.4f

Acidic soils typically yield blue or lavender-blue hydrangea blooms. Alkaline (basic) soil tends to grow pinkish-red blooms. If soil has a $[OH^-]$ of 6.3×10^{-7} *M*, what is pH of the soil and what colour blooms will this soil promote for hydrangeas growing in this soil?

Solution:

Given information: $[OH^-] = 6.3 \times 10^{-7}$ *M*

Asked to find: the pH of soil and, thus, the likely colour of the flower's blooms

Steps – First find pOH, then calculate pH. If acidic, blooms will be blue; if alkaline, blooms will be pink/red.

Step 1 – Calculate pOH using $\text{pOH} = -\log[OH^-]$

$\text{pOH} = -\log[6.3 \times 10^{-7}]$

$\text{pOH} = 6.20$

Step 2 – Find the pH and determine colour of the blooms

$\text{pH} = 14 - \text{pOH}$

$\text{pH} = 14 - 6.20$

$\text{pH} = 7.80$

Therefore the pH of the soil is 7.80, which is slightly alkaline, so the blooms will be a pinkish/red colour.

Source: "Example 16.4e" by Jackie MacDonald, CC BY-NC-SA 4.0

Exercise 16.4g

The hydronium ion concentration of vinegar is approximately 4×10^{-3} *M*. What is the pOH of this solution?

Check Your Answer[7] **Source: "Exercise 16.4g" by Jackie MacDonald, CC-BY-NC-SA 4.0**

Links to Interactive Learning Tools

Explore pH and pOH from the Physics Classroom.

Attribution & References

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Notes

1. (1) Basic; (2) Acidic; (3) Basic; (4) Neutral; (5) Acidic; (6) Basic
2. Part 1 (a) pOH = 4.75, basic; (b) pOH = 10.2, acidic; Part 2 (a) pH = 8.35, basic; (b) pH = 0.9, acidic
3. pH = 5.70

4. $[H_3O^+]$ = 12 *M*
5. Step 1: Find pOH using $\mathrm{pOH} = -\log[\mathrm{OH}^-]$; therefore, pOH = 1.04; pH = 14 - 1.04 = 12.96
6. Use the formula $[OH^-] = 10^{-pOH}$ to determine the hydroxide concentration of the bleach solution. $[OH^-] = 10^{-pOH}$ $[OH^-] = 10^{-12.35}$ $[OH^-] = 4.5 \times 10^{-13}$ *M*; since the pOH is higher than 7, this means its corresponding pH is below 7, and the solution is acidic.
7. Step 1: Find pH first using pH = -log$[H_3O^+]$; pH = 2.4; Step 2 calculate pOH: pOH = 14 - pH = 14 - 2.4 = 11.6

16.5 NEUTRALIZATION

Learning Objectives

By the end of this section, you will be able to:

- Describe a neutralization reaction.
- Predict whether a salt solution will be acidic, basic, or neutral.
- Perform calculations involving titrations of strong acids and strong bases.

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word "neutralization" seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own that affect the overall pH.

Acid-Base Neutralization

Recall the general chemical equation for a neutralization reaction:

$$\text{Acid} \ + \ \text{Base} \rightarrow \ \text{Salt} \ + \ \text{Water}$$

It is important to remember neutralization reactions are just a specific type of double displacement reaction.

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

- A strong acid and a strong base, such as $\text{HCl}(aq)$ and $\text{NaOH}(aq)$, react to form a neutral solution since they fully dissociate in water and their conjugate partners produced are of negligible strength:

$$\mathrm{HCl}(aq)\ +\ \mathrm{NaOH}(aq) \rightleftharpoons \mathrm{NaCl}(aq)\ +\ \mathrm{H_2O}(l)$$

- A strong acid and a weak base yield a weakly acidic solution, not because of the strong acid involved, but because of the conjugate acid of the weak base. A weak base produces a strong conjugate acid, and this will affect the overall pH to be more acidic.
- A weak acid and a strong base yield a weakly basic solution. A solution of a weak acid reacts with a solution of a strong base to form the conjugate base of the weak acid and the conjugate acid of the strong base. The conjugate acid of the strong base is a weaker acid than water and has no effect on the acidity of the resulting solution. However, the conjugate base of the weak acid is a weak base and ionizes slightly in water. This increases the amount of hydroxide ion in the solution produced in the reaction and renders it slightly basic.
- A weak acid plus a weak base can yield either an acidic, basic, or neutral solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. Occasionally the weak acid and the weak base will have the *same* strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral. To predict whether a particular combination will be acidic, basic or neutral, tabulated *K* values of the conjugates must be compared.
    - The **acid dissociation constant, (Ka)**, is an equilibrium constant that gives numerical representation of an acid's strength in a solution based its degree of dissociation in water. The greater the K_a, the stronger the acid.
    - The **base dissociation constant, (K_b)**, is an equilibrium constant that measures how completely a base dissociates into ions in water. The greater the Kb, the stronger the base.

Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$\mathrm{CaCO_3}(s)\ +\ 2\mathrm{HCl}(aq) \rightleftharpoons \mathrm{CaCl_2}(aq)\ +\ \mathrm{H_2O}(l)\ +\ \mathrm{CO_2}(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) \;+\; \mathrm{2OH^-}(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :

$$\mathrm{H_3O^+} \;+\; \mathrm{OH^-} \rightleftharpoons \mathrm{2H_2O}(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect.

Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in coordination with magnesium hydroxide to balance the side effects of the two substances.

Figure 16.5a Magic of Antacids: A jar of Antacids is shown. Antacids are bases, and are used to neutralize stomach acids by individuals experiencing acid reflux (credit: work by Midnightcomm, CC BY-SA 2.5).

Culinary Aspects of Chemistry

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 16.5b). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odour of the fish, and also adds a "sour" taste that we seem to enjoy.

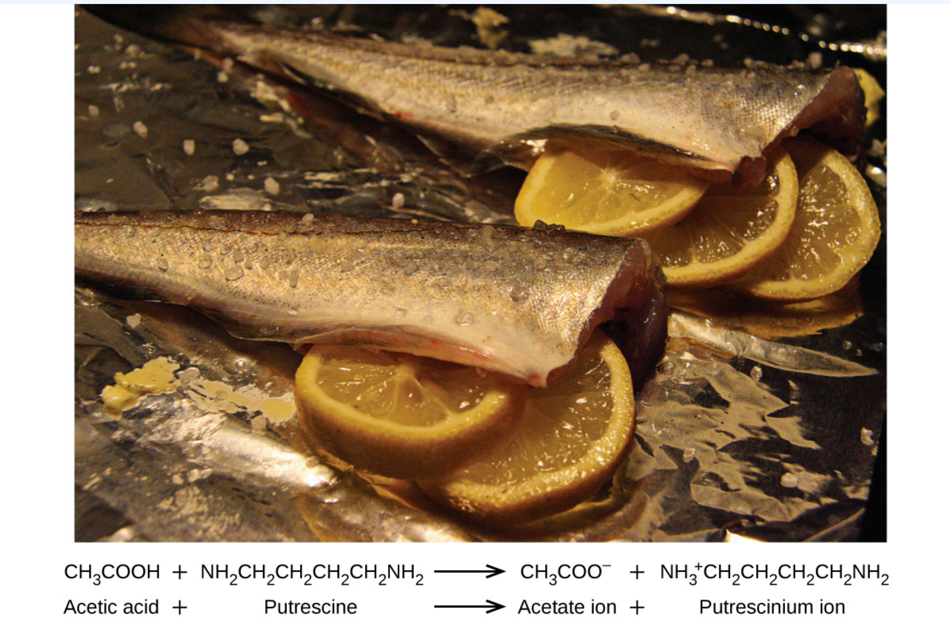

Figure 16.5b A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favours the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavour of the vegetables with the acid making them taste sour.

These cooking practices emerged from Peoples of the past. For example, many of these modern-day preparation and cooking practices steam from traditional Indigenous ingredients and techniques.

Indigenous Perspective: Indigenous Food Culture

Figure 16.5c Three sisters Garden: Three sisters planting (corn, beans, and squash) at a community garden is pictured. (credit: work by esagor, CC BY-NC 2.0.)

Launched in 2020 by the Indigenous Tourism Association of Canada (ITAC), the website, Destination Indigenous, brings awareness and mindfulness to the best Indigenous tourism experiences in Canada from Pacific coast to Arctic coast to Atlantic coast, including Indigenous food culture.

In an excerpt from Food & Culture – Indigenous Cuisine website (2020), food as part of an interdependent ecosystem is highlighted:

> "Traditional food sources were seen as part of a healthy and interdependent ecosystem. Indigenous [communities] traditionally only harvested, hunted or gathered what they needed to survive, and endeavoured to not let anything go to waste. In communities with abundant fish, for example, every edible part of the fish was eaten, including the head, eyes, offal and eggs.
>
> Inedible animal or plant material was often ingeniously repurposed for practical use. Animal bones could be used for tools, tanned hides and furs could be used for shelter and clothing, rawhide could be used for snowshoes, fishing nets or drum covers, and intestines or bladders could be used for cooking vessels or water storage. Plant materials, like spruce root or birch bark, could also be used for food storage." (*Food & Culture – Indigenous Cuisine*, 2020, para. 4).

Neutralization reactions of acids and bases are an important concept in many aspects of life. Conceptualizing the outcomes of acid base reactions is key to understanding the world around us.

Strong Acid-Strong Base Reactions

When a strong acid and a strong base are combined in stoichiometrically equivalent quantities – when $[H^+]$ equals $[OH^-]$ – a neutral solution results (pH = 7). The acid and base have neutralized each other, and the acidic and basic properties are no longer present. When equal amounts of a strong acid such as hydrochloric acid are mixed with a strong base such as sodium hydroxide, the result is a neutral solution. The products of the reaction do not have the characteristics of either an acid or a base. The balanced molecular equation is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H2O(l)$$

As discussed in chapter 14, chemical reactions occurring in aqueous solution are more accurately represented with a net ionic equation. The full ionic equation for the neutralization of hydrochloric acid by sodium hydroxide is written as follows:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

Since the acid and base are both strong, they are fully ionized and so are written as ions, as is the NaCl formed as a product. The sodium and chloride ions are spectator ions in the reaction, leaving the following as the net ionic reaction.

$$H^+ (aq) + OH^-(aq) \rightarrow H_2O(l)$$

All neutralization reactions of a strong acid with a strong base simplify to the net ionic reaction of hydrogen ion combining with hydroxide ion to produce water.

Watch Acid-Base Reaction (HCl + NaOH) (0min 56s).

What if the acid is a **diprotic acid** such as sulfuric acid? The balanced molecular equation now involves a 1:2 ratio between acid and base.

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$

In order for the reaction to be a full neutralization, twice as many moles of NaOH must react with the H_2SO_4. The sodium sulfate salt is soluble, and so the net ionic reaction is again the same. Different mole ratios occur for other polyprotic acids or bases with multiple hydroxides such as $Ca(OH)_2$.

Reactions Involving a Weak Acid or Weak Base

Salt solutions do not always neutralize to have a pH of 7. As a general concept, if a strong acid is mixed with a weak base, the resulting solution will be slightly acidic. If a strong base is mixed with a weak acid, the solution will be slightly basic. The reaction between weak nitrous acid and strong potassium hydroxide is shown below.

$$HNO_2(aq) + KOH(aq) \rightarrow KNO_2(aq) + H_2O(l)$$

In order to write the net ionic equation, the weak acid must be written as a molecule since it does not ionize to a great extent in water. The base and the salt are fully dissociated.

$$HNO_2(aq) + K^+(aq) + OH^-(aq) \rightarrow K^+(aq) + NO_2^-(aq) + H_2O(l)$$

The only spectator ion is the potassium ion, resulting in the net ionic equation:

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The strong hydroxide ion essentially “forces” the weak nitrous acid to become ionized. The hydrogen ion from the acid combines with the hydroxide ion to form water, leaving the nitrite ion as the other product. The resulting solution is not neutral, but instead is slightly basic.

Reactions can also involve a weak base and strong acid, resulting in a solution that is slightly acidic. The molecular and net ionic equations for the reaction of hydrochloric acid and ammonia are shown below.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq) \text{ (}Cl^-\text{is a spectator ion)}$$

Reactions between acids and bases that are both weak may result in solutions that are neutral, acidic, or basic.

Source: “Strong Acid-Strong Base Reactions” was adapted by Jackie MacDonald from “21.16: Neutralization Reaction and Net Ionic Equations for Neutralization Reactions” In *Introductory Chemistry (CK-12)* by CK-12 Foundation, shared under CK-12 license

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References

Food & Culture – Indigenous Cuisine. (2020, September 21). *DI – Culinary*.

16.6 TITRATIONS AND NEUTRALIZATION CALCULATIONS

Learning Objectives

By the end of this section, you will be able to:

- Explain the use of acid-base indicators in determining pH of a solution and outline how it is used in a titration experiment.
- Know the steps of an acid-base titration experiment.
- Perform neutralization calculations involving strong acids and strong bases.

In the previous section, neutralization reactions were introduced. This section will examine the basics of acid-base titrations and perform neutralization calculations between strong acids and strong bases.

Titrations

When hydrochloric acid is reacted with sodium hydroxide, an acid/base mole ratio of 1:1 is required for full neutralization.

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

If instead the hydrochloric acid were reacted with barium hydroxide, the mole ratio would be 2:1.

$$2\mathrm{HCl}(aq) + \mathrm{Ba(OH)_2}(aq) \rightarrow \mathrm{BaCl_2}(aq) + 2\mathrm{H_2O}(l)$$

Two moles of HCl are required to completely neutralize one mole of $Ba(OH)_2$. In a balanced neutralization equation, the moles of H^+ ions supplied by the acid will be equal to the moles of OH^- ions supplied by the base. The equivalence point is the point in a neutralization reaction when the number of moles of hydrogen ions is equal to the number of moles of hydroxide ions.

In the laboratory, you may need to determine the concentration of an acid or a base whose concentration is not known. This can be accomplished by performing a controlled neutralization reaction. A **titration** is an experiment in which a solution, whose concentration is known, is gradually added to a measured volume of another solution in order to determine its concentration. Typically, the **titrant** (the known solution) is added from a buret to a known volume of the **analyte** (the unknown concentration). Many titrations are acid-base neutralization reactions, although other types of titrations can also be performed.

In order to perform an acid-base titration, the chemist must have a way to visually detect that the neutralization reaction has reached the equivalence point. An indicator is a substance that has a distinctly different colour when in an acidic or basic solution. A commonly used indicator for strong acid-strong base titrations is phenolphthalein. Solutions in which a few drops of phenolphthalein have been added, turn from colourless to brilliant pink as the solution turns from acidic to basic (Figure 16.6a).

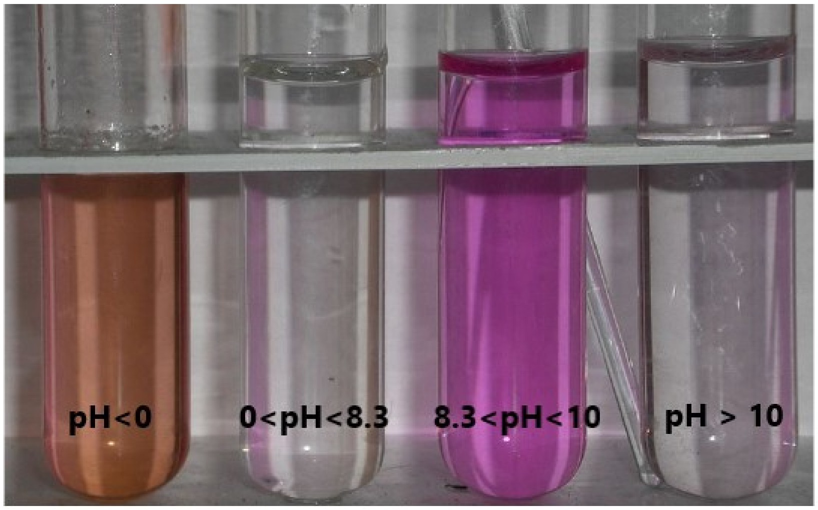

Figure 16.6a Phenolphthalein at different pH: Four test tubes are shown containing solutions at various pH, all containing the pH indicator, phenolphthalein. From left to right: At a pH less than zero, phenolphthalein will turn orange, as shown in the first test tube on the left. At a pH between 0 and 8.3, the solution will remain clear. A solution between a pH of zero to 8.3 through 10, the solution will be pink. Finally a solution with this indicator will be clear for any solutions with a pH greater than 10. Exact pH ranges of this indicator are provided by the supplier when purchased used in lab (credit: modification of work by Siegert, PD / pH ranges corrected by Jackie MacDonald)**.**

The steps in a titration reaction are outlined below.

1. A measured volume of an acidic solution (the analyte) whose concentration is unknown is added to an Erlenmeyer flask.
2. Several drops of an indicator are added to the acid and mixed by swirling the flask.
3. A buret is filled with a basic solution (the titrant) of known molarity.
4. The stopcock of the buret is opened and base is slowly added to the acid while the flask is constantly swirled to ensure mixing. The stopcock is closed at the exact point at which the indicator just changes colour. If the colour change does not remain after swirling, the neutralization reaction has not yet reached completion.

The standard solution is the solution in a titration whose concentration is known. In the titration described above, the base solution is the standard solution. It is very important in a titration to add the solution from the buret slowly so that the point at which the indicator changes colour can be found accurately. The end point of a titration is the point at which the indicator changes colour. When phenolphthalein is the indicator, the end point will be signified by a faint pink colour.

Watch **Setting Up and Performing a Titration (6min 52sec)**.

Other pH indicators behave in essentially the same way.

Watch What Are Indicators & How Do We Use Them? | Chemical Tests | Chemistry | FuseSchool (3min 18s).

Neutralization Calculations

As shown at the beginning of this section, when hydrochloric acid is reacted with sodium hydroxide, an acid/base mole ratio of 1:1 is required for full neutralization as shown in the balance chemical equation below:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

However, as we have learned, not all acids and bases neutralize at a one to one mole ratio. When a strong diprotic or triprotic acid or base is used in a titration neutralization reaction, the mole ratio needs to be taken into consideration when performing calculations. Let's reexamine the neutralization of hydrochloric acid with diprotic barium hydroxide:

$$2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$$

Two moles of HCl are required to completely neutralize one mole of $Ba(OH)_2$. The strong acid, HCl, furnishes 1 H^+ ion; whereas, $Ba(OH)_2$ ionizes 2 OH^- ions. In a balanced neutralization equation, the moles of H^+ ions supplied by the acid is equal to the moles of OH^- ions supplied by the base. The equivalence point is the point in a neutralization reaction when the number of moles of hydrogen ions is equal to the number of moles of hydroxide ions.

> Therefore, it is of utmost importance that students consider mole ratios of the acid and base in their calculations when performing neutralization calculations.

There are different ways to solve neutralization problems: solving neutralization problems using stoichiometry will be outlined in this section.

Performing Stoichiometric Calculations to Solve Neutralization Problems

Take a closer look at Figure 16.6b, which is a modified version of Figure 9.2a from 9.2 – Mole-Mass and Mass-Mass Calculations. Focus your attention on the four rectangles inside the red coloured outline. These provide a flowchart on the steps needed to solve a neutralization reaction problem.

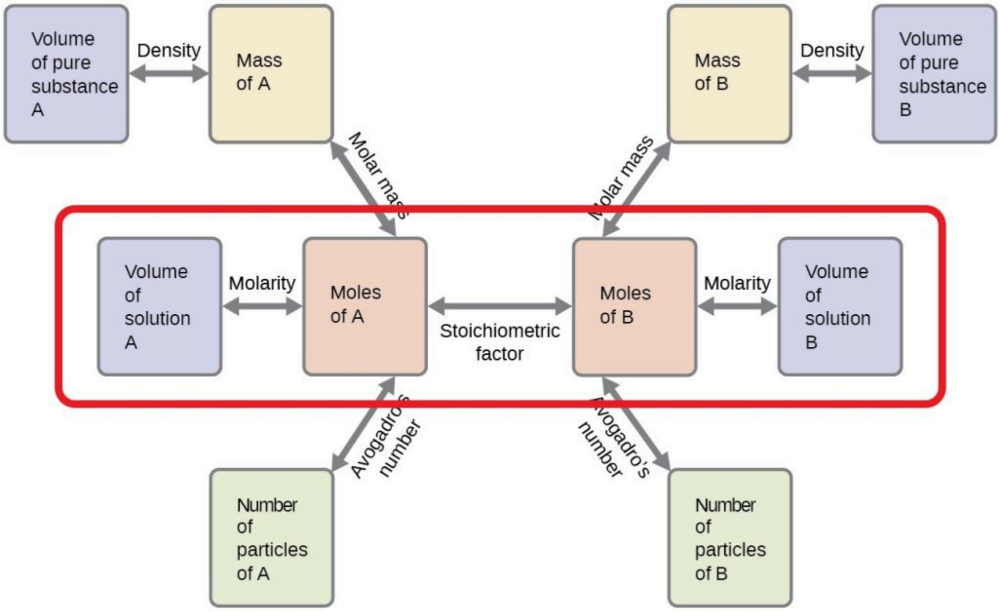

Figure 16.6b Stoichiometry Flowchart for Neutralization Calculations. (Image Source: General Chemistry 1 & 2, CC BY 4.0). (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Calculating the Unknown Molarity of an Acid/Base in a Neutralization Reaction:

Follow the steps below to solve for an unknown molarity.

- Take known volume of known solution "A" and multiply it by molarity of solution A to calculate the moles of A.
- Next, apply the mole ratio calculation to determine the moles of solution B.
- Finally, apply the final stoichiometric calculation using the moles of solution B and given volume of solution B to calculate the molarity of solution B needed to neutralize solution A.

Example 16.6a

In a titration of hydrochloric acid with barium hydroxide, 32.00 mL of 0.150 *M* HCl is required to neutralize 26.75 mL of the barium hydroxide solution. Calculate the molarity of the barium hydroxide solution. (Remember, you must work in litres for volume since you are performing mole calculations using units of molarity, which are moles/L).

Solution

Step 1: List the known values, write the balanced chemical equation, and and plan the problem.

Known

- molarity of the HCl solution = 0.150 *M*
- volume of the HCl solution = 32.00 mL = 0.03200L
- volume of the $Ba(OH)_2$ solution = 26.75 mL = 0.02675L
- Balanced Chemical Equation: $2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$
- Mole ratio of acid to base in balanced chemical equation is 2:1

Unknown

- molarity of the $Ba(OH)_2$ solution = ?

Step 2 : Determine the moles of HCl that were consumed in the reaction.

- mol HCl = $M \times L = 0.150 M \times 0.03200 L$ = 0.00480 mols of HCl

Step 3: From the mole ratio, calculate the moles of $Ba(OH)_2$ that reacted.

- mol $Ba(OH)_2$ = 0.00480 mols HCl x [1 mol $Ba(OH)_2$ / 2 mol HCl] = 0.00240 mols = 2.40×10^{-3} mols of $Ba(OH)_2$

Step 4: Determine the molarity of $Ba(OH)_2$ by dividing the moles by the volume.

- $[Ba(OH)_2]$ = 2.40×10^{-3} mols / 0.02675 L = 0.0897 *M*

Therefore the molarity of the basic barium hydroxide solution needed to neutralize the acid solution is 0.0897 *M* or 8.97×10^{-2} *M*.

Source: "Example 16.6a" by Jackie MacDonald, licensed under CC BY-NC 4.0

Example 16.6b

Suppose that a titration is performed between a strong acid and strong base: 20.70 mL of 0.500 *M* NaOH is required to reach the end point when titrated against 15.00 mL of HBr of unknown concentration. Use the neutralization equation to determine the concentration of hydrobromic acid used in this titration.

Solution

Step 1: List the known values, write the balanced chemical equation, and and plan the problem.

Known

- molarity of the NaOH solution = 0.500 *M*
- volume of the NaOH solution = 20.70 mL
- volume of the HBr solution = 15.00 mL
- Balanced Chemical Equation: $HBr(aq) + NaOH(aq) \rightarrow NaBr(aq) + H_2O(l)$
- Mole ratio of acid to base in balanced chemical equation is 1:1.

Unknown

- molarity of the HBr solution = ?

Step 2 : Determine the moles of HBr that were consumed in the reaction.

- mol NaOH = $M \times L = 0.500 M \times 20.70 L$ = 0.01035 mols of NaOH

Step 3: From the mole ratio, calculate the moles of HBr that reacted.

- mol HBr = 0.01035 mols NaOH x [1 mol HBr / 1 mol NaOH] = 0.01035 mols HBr = 1.035×10^{-2} mols HBr

Step 4: Determine the molarity of HBr by dividing the moles by the volume.

- [HBr] = 1.035×10^{-2} mols / 0.015 L = 0.690 *M* HBr

Therefore the molarity of the Hydrobromic acid solution needed to neutralize the base solution is 0.690 *M*.

Source: "Example 16.6b" by Jackie MacDonald, licensed under CC BY-NC 4.0

Exercise 16.6a

35.00 mL of 0.125 *M* HCl is required to neutralize 25.00 mL of KOH. Determine the concentration of the base solution.

Check Your Answer[1]

Exercise 16.6b

15.75 mL of 0.350 *M* H_2SO_4 is required to neutralize 10.00 mL of NaOH. Determine the concentration of the sodium hydroxide solution.

Check Your Answer[2]

Source: "Exercise 16.6b" by Jackie MacDonald is licensed under CC BY-NC 4.0.

Calculating the Unknown Volume of an Acid/Base in a Neutralization Reaction:

If you are asked to solve for an unknown volume of an acid or base in a neutralization reaction problem, follow these steps:

- Take known volume of known solution "A" and multiply it by molarity of solution A to calculate the moles of A.
- Next, apply the mole ratio calculation to determine the moles of solution B.
- Finally, apply the final stoichiometric calculation using the moles of solution B and given molarity of solution B to calculate the volume of solution B needed to neutralize solution A.

Example 16.6c

What volume, in mL, of a 0.139 *M* solution of barium hydroxide is required to neutralize 45.00 mL of 0.256 *M* HCl?

Solution

Step 1: List the known values, write the balanced chemical equation, and plan the problem.

Known

- molarity of the HCl solution = 0.256 *M*
- volume of the HCl solution = 45.00 mL = 0.04500 L
- molarity of the $Ba(OH)_2$ solution = 0.139 *M*
- Balanced Chemical Equation: $2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$
- Mole ratio of acid to base in balanced chemical equation is 2:1.

Unknown

- volume of the $Ba(OH)_2$ solution = ?

Step 2 : Determine the moles of HCl that were consumed in the reaction.

- mol HCl = *M* × L = 0.256 *M* × 0.04500 L = 0.01152 mols of HCl

Step 3: From the mole ratio, calculate the moles of $Ba(OH)_2$ that reacted.

- mol $Ba(OH)_2$ = 0.01152 mols HCl x [1 mol $Ba(OH)_2$ / 2 mol HCl] = 0.00576 mols = 5.76×10^{-3} mols of $Ba(OH)_2$

Step 4: Determine the volume of $Ba(OH)_2$ using moles and molarity of $Ba(OH)_2$.

- $[Ba(OH)_2]$ = 5.76×10^{-3} mols x 1 L / 0.139 mols = 0.0414 L

Final Step: Convert volume to mL

- 0.0414 L x 1000 mL/ 1L = 41.4 mL

Therefore 41.4 mL of the barium hydroxide solution is needed to neutralize 45.00 mL of 0.256 *M* HCl.

Source: "Example 16.6c" by Jackie MacDonald, licensed under CC BY-NC 4.0

Exercise 16.6c

What volume, in mL, of a 0.500 M solution of sodium hydroxide would be required to neutralize 40.0 mL of a 0.375 M H_2SO_4 solution?

Check Your Answer[3] Source: "Exercise 16.6c" by Jackie MacDonald, licensed under CC BY-NC 4.0

Attribution & References

Except where otherwise noted, this page is adapted by Jackie MacDonald from "21.4 Acid-Base Neutralization" In *CK-12 Chemistry – Intermediate* by CK-12, licensed under CK-12 Curriculum Materials license.

Notes

1. 0.175 M KOH
2. 0.276 M NaOH
3. *Step 1: List the known values, write the balanced chemical equation, and plan the problem.* Known

    - molarity of the H_2SO_4 solution = 0.375 M
    - volume of the H_2SO_4 solution = 40.0 mL = 0.0400 L
    - molarity of the NaOH solution = 0.500 M
    - Balanced Chemical Equation: $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
    - Mole ratio of acid to base in balanced chemical equation is 1:2.

    Unknown

    - volume of the H_2SO_4 solution = ?

    Step 2 : Determine the moles of H_2SO_4 that were consumed in the reaction.

    - mol H_2SO_4 = M × L = 0.375 M × 0.0400 L = 0.0150 mols of H_2SO_4

    Step 3: From the mole ratio, calculate the moles of NaOH that reacted.

- mol NaOH = 0.0150 mols H_2SO_4 x [2 mol NaOH / 1 mol H_2SO_4] = 0.0300 mols = 3.00 x 10^{-2} mols of NaOH

Step 4: Determine the volume of NaOH using moles and molarity of NaOH.

- [NaOH] = 3.00 x 10^{-2} mols x 1 L / 0.500 mols = 0.0600 L

Final Step: Convert volume to mL

- 0.0600 L x 1000 mL/ 1L = 60.0 mL

Therefore 60.0 mL of the sodium hydroxide solution is needed to neutralize 40.0 mL of a 0.375 *M* H_2SO_4 solution.

16.7 BUFFERS

Learning Objectives

By the end of this section, you will be able to:

- Define buffer and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M $HCl(aq)$] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9 — a pH that is not conducive to life. Fortunately, the body has a mechanism for minimizing such dramatic pH changes. This mechanism involves a buffer, a solution that resists dramatic changes in pH.

Watch Buffers, the Acid Rain Slayer: Crash Course Chemistry #31 (11min 40s).

Buffers resist dramatic changes in pH by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid, or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate ($NaC_2H_3O_2$, a salt derived from that acid). Another example of a buffer is a solution containing ammonia (NH_3, a weak base) and ammonium chloride (NH_4Cl, a salt derived from that base).

Characteristics of a Good Buffer

Good buffering systems have the following characteristics:

- The solution contains a weak acid and its conjugate base OR a weak base and its conjugate acid

- The buffer resists changes in pH by reacting with added acid or base, so these ions do not accumulate.
- Any added acid reacts with the conjugate base to resist pH changes
- Any added base reacts with the conjugate acid to resist pH changes

Buffers cannot be made from a strong acid (or strong base) and its conjugate since these solutions ionize completely in water. Also take note, water is not a buffer.

Source: “Characteristics of a Good Buffer” by Jackie MacDonald, CC BY-NC-4.0

How Buffers Work

Let’s consider an acetic acid – sodium acetate buffer to demonstrate how buffers work. If a strong base — a source of OH−(*aq*) ions — is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(l) + C_2H_3O_2^-(aq)$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+(aq)+C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq)$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid.

In chemistry texts and sources, you may have noticed that H^+ and H_3O^+ are used interchangeably in contexts when the proton donor-acceptor mechanism does not need to be emphasized. Since it is easier to write the H^+ proton, chemists often use it to represent acid-base reactions or to explain general concepts in buffering systems. Thus, it is permissible to talk about “hydrogen ions” and use the formula H^+ in writing chemical equations as long as you remember that they are not to be taken literally in the context of aqueous solutions.

Source: “The Hydronium Ion” by Stephen Lower & Avneet Kahlon In *Acids and Bases in Aqueous Solutions*, licensed under CC BY 3.0.

Figure 16.7a illustrates both actions of the acetic acid – sodium acetate buffer.

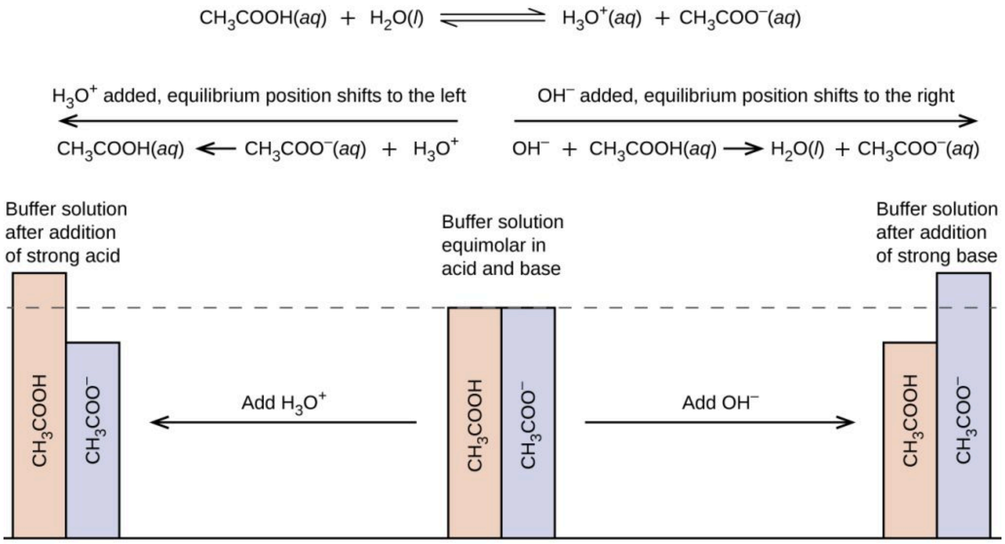

Figure 16.7a Buffering Action of Acetic Acid and Sodium Acetate: Whether a small amounts of strong acid or base are added to this buffer system, the pH does not drastically change due to its ability to form more weak acid or more conjugate base depending on whether acid or base is added to the system. (credit: *General Chemistry 1 & 2*, CC BY 4.0),

Figure 16.7b illustrates a basic summary of the action of buffers when small amounts of strong base and acid is added.

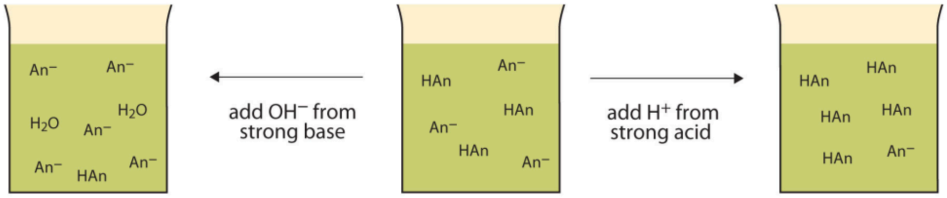

Figure 16.7b Generalizing the Actions of Buffers: "HAn" represents the weak Acid. "An^{-}" represents the conjugate base of the weak acid. If strong acid is added to buffer, the system shifts to the right to produce more weak acid, which holds pH steady. If a strong base is added to the buffer, the system shifts to the right forming water and more weak acid, which also holds the pH constant (credit: *Map: Introductory Chemistry (Tro)*, CK-12 license)

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

while the ammonium ion, $NH_4^+(aq)$ can react with any hydroxide ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$

Example 16.7a

Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. CH_3NH_2 and CH_3NH_3Cl
4. NH_3 and NaOH

Solution

1. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid—the formate ion (CHO_2^-). The combination of these two solutes would make a buffer solution.
2. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
3. Methylamine (CH_3NH_2) is like ammonia with one of its hydrogen atoms substituted with a CH_3 (methyl) group. Because it is not on our list of strong bases, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 16.7a

Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.

1. $NaHCO_3$ and NaCl
2. H_3PO_4 and NaH_2PO_4
3. NH_3 and $(NH_4)_3PO_4$
4. NaOH and NaCl

Check Your Answer[1]

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain capacity. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Buffered Aspirin

Many people are aware of the concept of buffers from buffered aspirin. Aspirin is well known as a pain reliever and fever reducer. Buffered aspirin contains aspirin (acetylsalicylic acid) and also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt regulates the acidity of the aspirin to minimize its acidic side effects in the stomach. The salt acts like a base, while aspirin is itself a weak acid due to its carboxylic acid group. The H atom in that group can be donated, and therefore, aspirin can act as a Brønsted-Lowry acid. Figure 16.7c and 16.7d show the molecular structure of aspirin in 3D and 2D.

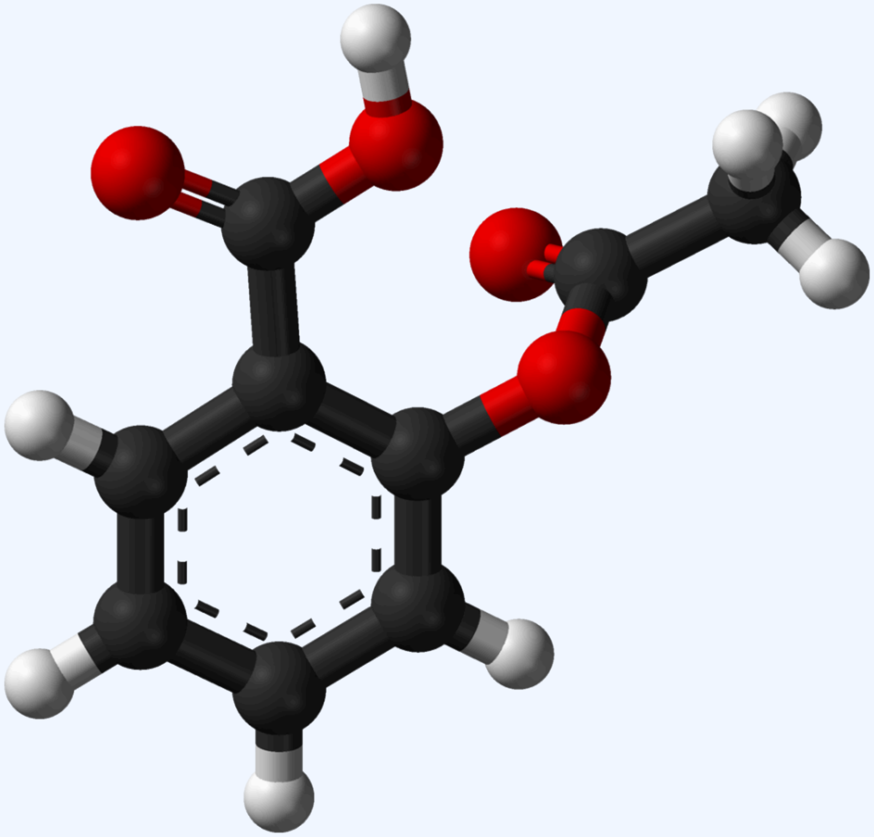

Figure 16.7c 3D Ball and Stick Molecular Structure of Aspirin: Aspirin (acetylsalicylic acid) is an aromatic compound containing both a carboxylic acid functional group and an ester functional group rendering it is a weak acid that is only slightly soluble in water. (credit: work by Ben Mills, PD).

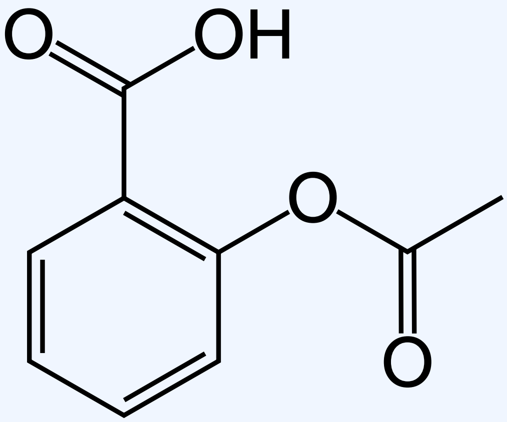

Figure 16.7d Skeletal 2D Image of Aspirin: Aspirin (acetylsalicylic acid) is an aromatic compound containing both a carboxylic acid functional group and an ester functional group rendering it is a weak acid. (credit: work by Ben Mills, PD).

Links to Interactive Learning Tools

Explore Learn the Basics about Buffers from eCampusOntario H5P Studio.

Attribution & References

Except where otherwise noted, this page is adapted by Jackie MacDonald from a section in "14.10: Buffers-Solutions that Resist pH Change" In *Map: Introductory Chemistry (Tro)* by Marisa Alviar-Agnew & Henry Agnew, shared under a CK-12 license.

References

Stephen Lower & Avneet Kahlon. (2022, August 10). *The Hydronium Ion*. Chemistry LibreTexts.

Notes

1.
    1. No; $NaHCO_3$ and NaCl are not acid/base conjugate pairs;
    2. Yes;
    3. Yes; H_3PO_4 is a weak acid and NaH_2PO_4 is a salt of its conjugate base;
    4. No - NaOH is a strong base, a buffer requires a weak base or acid and its conjugate.

CHAPTER 16 - SUMMARY

16.1 Acids and Bases

A summary of key properties and characteristics of acids and bases commonly encountered in everyday life was provided.

- Both acids and bases release ions in water solution.
- Since both are capable of producing ions when dissolved in water, they are electrolytes.
- Since they are electrolytes, they are both capable of conducting electricity.
- Both acids and bases undergo neutralization reaction

Strong acids and bases are 100% ionized in aqueous solution. Weak acids and bases are less than 100% ionized in aqueous solution. Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions. A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H3O+, and the hydroxide ion, OH– depending on what it is reacting with.

16.2 Ionization of Water

An acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2H_2O(l) \leftrightharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25\ ^\circ C$$

16.3 Reactions in Acids and Bases

Chemical reactions are classified according to similar patterns of behaviour. Acid-base reactions involve the transfer of hydrogen ions between reactants.

General acid-base reactions, also called neutralization reactions can be summarized with the following reaction equation:

$$\text{ACID}(aq) + \text{BASE}(aq) \rightarrow H_2O(l) + \text{SALT}(aq) \text{ or } (s)$$

- The DRIVING FORCE for a general acid-base reaction is the formation of water.

Gas-forming acid-base reactions can be with carbonates or metals. One example of an acid mixing with a carbonate is summarized in the following reaction equation:

$$\text{ACID}(aq) + NaHCO_3 \text{ or } Na_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g) + \text{SALT}(aq) \text{ or } (s)$$

- The DRIVING FORCE for a gas-forming acid-base reaction is the formation of gas.

Reactions of acids with metal oxides results in the formation of salt and water.

16.4 Introduction to pH and pOH

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7} M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7} M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\text{pH} = -\log[H_3O^+]$. The concentration of OH^- can be expressed as the pOH of the solution: $\text{pOH} = -\log[OH^-]$. In pure water, pH = 7.00 and pOH = 7.00.

16.5 Neutralization

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. A strong acid will neutralize a strong base and result in a neutral solution. However, some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic.

16.6 Titrations and Neutralization Calculations

Acids and bases neutralize each other, forming a salt and water. A strong acid-strong base neutralization results in a neutral solution with a pH of 7. A titration is an experiment in which a controlled acid-base neutralization reaction is used to determine the unknown concentration of an acid or a base. The equivalence point is reached when the number of hydrogen ions is equal to the number of hydroxide ions. Acid-base indicators are used in a titration in order to detect the end point of the titration. Neutralization calculations can be performed to determine the concentration or volume of a strong acid or base used in a titration.

16.7 Buffers

Buffering systems have the following characteristics:

- The solution contains a weak acid and its conjugate base OR a weak base and its conjugate acid
- The buffer resists changes in pH by reacting with added acid or base, so these ions do not accumulate.
- Any added acid reacts with the conjugate base to resist pH changes
- Any added base reacts with the conjugate acid to resist pH changes

Buffers cannot be made from a strong acid (or strong base) and its conjugate since these solutions ionize completely in water. Also recognize that water is not a buffer.

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- "16.4 Introduction to pH and pOH" & "16.5 Neutralization" summaries from "Chapter 14 Summary"

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CHAPTER 16 - REVIEW

16.1 Acids and Bases

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.
   Check answers: [1]
2. Write equations that show $H_2PO_4{}^-$ acting both as an acid and as a base.
   Check answers: [2]
3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:
   a. H_3O^+
   b. HCl
   c. NH_3
   d. CH_3CO_2H
   e. $NH_4{}^+$
   f. $HSO_4{}^-$
   Check answers: [3]
4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:
   a. HNO_3
   b. $PH_4{}^+$
   c. H_2S
   d. CH_3CH_2COOH
   e. $H_2PO_4{}^-$
   f. HS^-
   Check answers: [4]
5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
   a. H_2O
   b. OH^-
   c. NH_3
   d. CN^-
   e. S^{2-}
   f. $H_2PO_4{}^-$
   Check Answers: [5]
6. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
   a. HS^-

   b. $PO_4{}^{3-}$
   c. $NH_2{}^{-}$
   d. O^{2-}
   e. $H_2PO_4{}^{-}$

   Check Answers: [6]

7. What is the conjugate acid of each of the following? What is the conjugate base of each?
   a. OH^{-}
   b. H_2O
   c. $HCO_3{}^{-}$
   d. NH_3
   e. $HSO_4{}^{-}$
   f. H_2O_2
   g. HS^{-}
   h. $H_5N_2{}^{+}$

   Check Answers: For the following the conjugate acid is written first followed by its conjugate base: [7]

8. What is the conjugate acid of each of the following? What is the conjugate base of each?
   a. H_2S
   b. $H_2PO_4{}^{-}$
   c. PH_3
   d. HS^{-}
   e. $HSO_3{}^{-}$
   f. $H_3O_2{}^{+}$
   g. H_4N_2
   h. CH_3OH

   Check Answers: [8]

9. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:
   a. $HNO_3 + H_2O \longrightarrow H_3O^{+} + NO_3{}^{-}$
   b. $CN^{-} + H_2O \longrightarrow HCN + OH^{-}$
   c. $H_2SO_4 + Cl^{-} \longrightarrow HCl + HSO_4{}^{-}$
   d. $HSO_4{}^{-} + OH^{-} \longrightarrow SO_4{}^{2-} + H_2O$
   e. $O^{2-} + H_2O \longrightarrow 2OH^{-}$
   f. $[Cu(H_2O)_3(OH)]^{+} + [Al(H_2O)_6]^{3+} \longrightarrow Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$
   g. $H_2S + NH_2{}^{-} \longrightarrow HS^{-} + NH_3$

   Check Answer: [9]

10. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:
    a. ${NO_2}^- + H_2O \longrightarrow HNO_2 + OH^-$
    b. $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
    c. $HS^- + H_2O \longrightarrow H_2S + OH^-$
    d. $H_2{PO_4}^- + OH^- \longrightarrow {HPO_4}^{2-} + H_2O$
    e. $H_2{PO_4}^- + HCl \longrightarrow H_3PO_4 + Cl^-$
    f. $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$
    g. $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

    Check Answers: [10]
11. What are amphiprotic species? Illustrate with suitable equations.

    Check Answers: [11]
12. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.
    a. NH_3
    b. ${HPO_4}^-$
    c. Br^-
    d. ${NH_4}^+$
    e. ${ASO_4}^{3-}$

    Check Answers: [12]

16.2 Reactions of Acids and Bases

1. The following salts were produced in an acid-base neutralization reaction. Write the formulas and names of the acid and base from which each of these salts are formed.
    a. NaCl
    b. $MgCl_2$
    c. Na_2SO_4
    d. $NaNO_3$
    e. K_3PO_4

    Check Answers: [13]
2. When an acid reacts with carbonates what are the characteristic products?
3. Predict the products of a reaction of hydrobromic acid with sodium carbonate: $Na_2CO_3(s) + 2HBr(aq)$ →

    Check Answers: [14]
4. What is the generic formula for the oxidation of metals in acidic solutions?

Check Answers: [15]

5. Predict the products of a reaction of hydrochloric acids with magnesium metal.
   Check Answers: [16]
6. What is the generic formula for when a metal oxide reacts with an acid?
   Check Answers: [17]
7. Predict the products of a reaction of nitric acid with the metal oxide, copper oxide:
   Check Answers: [18]

16.3 Ionization of Water

1. Write an equation to show the autoionization of water.
   Check Answers: [19]
2. Calculate the $[H^+]$ for a solution at 25°C that is 1.0×10^{-5} M OH^-. Is this solution acidic, neutral or basic?
   Check Answers: [20]
3. Calculate the $[OH^-]$ for a solution at 25°C that is 2.0×10^{-2} M H^+. Is this solution acidic, neutral or basic?
   Check Answers: [21]
4. Calculate the $[H^+]$ for a solution at 25°C that is 1.0×10^{-7} M OH^-. Is this solution acidic, neutral or basic?
   Check Answers: [22]
5. Is the self ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40°C and 9.3×10^{-14} at 60°C.
   Check Answer: [23]

16.4 Introduction to pH and pOH

1. Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7} M$. K_w is 2.9×10^{-14} at 40 °C.
   Check Answers: [24]
2. The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.
   Check Answers: [25]
3. The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.
   Check Answers: [26]

4. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:
    a. 0.200 *M* HCl
    b. 0.0143 *M* NaOH
    c. 3.0 *M* HNO_3
    d. 0.0031 *M* $Ca(OH)_2$
    Check Answers: [27]
5. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:
    a. 0.000259 *M* $HClO_4$
    b. 0.21 *M* NaOH
    c. 0.000071 *M* $Ba(OH)_2$
    d. 2.5 *M* KOH
    Check Answers: [28]
6. What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?
    Check Answers: [29]
7. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?
    Check Answers: [30]
8. Calculate the hydrogen ion concentration and the hydroxide ion concentration in a red wine with a pH of 3.500.
    Check Answers: [31]
9. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice with a pH of 2.00.
    Check Answers: [32]
10. The hydronium ion concentration in a sample of rainwater is found to be 1.7×10^{-6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?
    Check Answers: [33]
11. The hydroxide ion concentration in household ammonia is 3.2×10^{-3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?
    Check Answers: [34]

16.5 Neutralization and 16.6 Titrations and Neutralization Calculations

1. 35.00 mL of 0.125 *M* HCl is required to neutralize 25.00 mL of KOH. Determine the concentration of the base solution.
    Check Answers: [35]

2. Suppose that a titration is performed between a strong acid and strong base: 20.70 mL of 0.500 *M* NaOH is required to reach the end point when titrated against 15.00 mL of HCl of unknown concentration. Determine the concentration of hydrochloric acid used in this titration.
   Check Answers: [36]
3. What is the concentration of a $Ba(OH)_2$ solution, if 17.25 mL is required to neutralize 19.10 mL of 0.520 *M* HBr?
   Check Answers: [37]
4. In a titration of sulfuric acid with sodium hydroxide, 32.20 mL of 0.250 M NaOH is required to neutralize 26.60 mL of the H_2SO_4 solution. Calculate the molarity of the sulfuric acid.
   Check Answers: [38]
5. What volume of 0.975 *M* NaOH is needed to neutralize 45.0 mL of 0.225 *M* sulfuric acid, H_2SO_4?
   Check Answers: [39]
6. What volume of 0.202 *M* HNO_3 is required to neutralize each of the following solutions?
   a. 15.5 mL of 0.155 *M* NaOH
   b. 25.1 mL of 0.0391 *M* $Ba(OH)_2$
      Check Answers: [40]

16.7 Buffers

1. Define buffer. What two related chemical components are required to make a buffer?
   Check Answers: [41]
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
   Check Answers: [42]
3. Of the following options (a – d), which combinations of compounds can make a buffer? Assume aqueous solutions.
   a. HCl and NaCl
   b. HNO_2 and $NaNO_2$
   c. NH_4NO_3 and HNO_3
   d. NH_4NO_3 and NH_3
      Check Answers: [43]
4. For each combination in previous question that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
   Check Answers: [44]

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Notes

1. One example for NH_3 as a conjugate acid: $NH_2{}^- + H^+ \longrightarrow NH_3$; as a conjugate base: $NH_4{}^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$
2. One example for $H_2PO_4{}^-$ behaving as an acid (proton donor): $H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$; One example for $H_2PO_4{}^-$ acting as a base (proton acceptor): $H_2PO_4^-(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + OH^-(aq)$
3. (a) $H_3O^+(aq) \longrightarrow H^+(aq) + H_2O(l)$; (b) $HCl(l) \longrightarrow H^+(aq) + Cl^-(aq)$; (c) $NH_3(aq) \longrightarrow H^+(aq) + NH_2{}^-(aq)$; (d) $CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2{}^-(aq)$; (e) $NH_4{}^+(aq) \longrightarrow H^+(aq) + NH_3(aq)$; (f) $HSO_4{}^-(aq) \longrightarrow H^+(aq) + SO_4{}^{2-}(aq)$
4. (a) $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$; (b) $PH_4^+(aq) \rightarrow H^+(aq) + PH_3(aq)$; (c) $H_2S(aq) \rightarrow H^+(aq) + HS^-(aq)$; (d) $CH_3CH_2COOH(aq) \rightarrow H^+(aq) + CH_3CH_2COO^-(aq)$; (e) $H_2PO_4^-(aq) \rightarrow H^+(aq) + HPO_4^{2-}(aq)$; (f) $HS^-(aq) \rightarrow H^+(aq) + S^{2-}(aq)$
5. (a) $H_2O(l) + H^+(aq) \longrightarrow H_3O^+(aq)$; (b) $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$; (c) $NH_3(aq) + H^+(aq) \longrightarrow NH_4{}^+(aq)$; (d) $CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)$; (e) $S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq)$; (f) $H_2PO_4{}^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)$
6. (a) $HS^-(aq) + H^+(aq) \rightarrow H_2S(aq)$; (b) $PO_4{}^{3-} + H^+(aq) \rightarrow HPO_4^{2-}(aq)$; (c) $NH_2{}^- + H^+(aq) \rightarrow NH_3(aq)$; (d) $O^{2-}(aq) + H^+(aq) \rightarrow OH^-(aq)$; (e) $H_2PO_4{}^- + H^+(aq) \rightarrow H_3PO_4(aq)$
7. (a) H_2O, O^{2-}; (b) H_3O^+, OH^-; (c) H_2CO_3, $CO_3{}^{2-}$; (d) $NH_4{}^+$, $NH_2{}^-$; (e) H_2SO_4, $SO_4{}^{2-}$; (f) $H_3O_2{}^+$, $HO_2{}^-$; (g) H_2S; S^{2-}; (h) $H_6N_2{}^{2+}$, H_4N_2

8. (a) H_3S^+, HS^-; (b) H_3PO_4, HPO_4^{2-}; (c) PH_4^+, PH_2^-; (d) H_2S, S^{2-}; (e) H_2SO_3, SO_3^{2-}; (f) $H_4O_2^{2+}$, H_2O_2; (g) $H_5N_2^+$, $H_3N_2^-$; (h) $CH_3OH_2^+$; CH_3O^- (Watch the video "14.8h | How to find the conjugate acid and conjugate base of CH3OH" for an explanation of the answer for (h))
9. The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) HNO_3(BA), H_2O(BB), H_3O^+(CA), $NO_3{}^-$ (CB); (b) CN^-(BB), H_2O(BA), HCN(CA), OH^-(CB); (c) H_2SO_4(BA), Cl^-(BB), HCl(CA), $HSO_4{}^-$ (CB); (d) $HSO_4{}^-$ (BA), OH^-(BB), $SO_4{}^{2-}$ (CB), H_2O(CA); (e) O^{2-}(BB), H_2O(BA) OH^-(CB and CA); (f) $[Cu(H_2O)_3(OH)]^+$(BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); (g) H_2S(BA), $NH_2{}^-$ (BB), HS^-(CB), NH_3(CA)
10. The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) NO_2^-(BB), H_2O (BA), HNO_3 (CA), OH^-(CB); (b) HBr (BA), H_2O (BB), Br^- (CB), H_3O^+ (CA); (c) HS^- (BB), H_2O (BA), H_2S (CA), OH^- (CB); (d) $H_2PO_4^-$ (BA), OH^- (BB), HPO_4^{2-} (CB), H_2O (CA); (e) $H_2PO_4^-$ (BB), HCl (BA), H_3PO_4 (CA), Cl^- (CB); (f) $[Fe(H_20)_5(OH)]^{2+}$ (BB), $[Al(H_2O)_6]^{3+}$ (BA), $[Fe(H_20)_6]^{3+}$ (CA), $[Al(H_2O)_5(OH)]^{2+}$ (CB); (View the video "14.10f | How to identify the conjugate acid-base pairs in [Fe(H2O)5(OH)]2+ + [Al(H2O)6]3+" for an explanation of the answer for (f): ; (g) CH_3OH (BA), H^- (BB), CH_3O^- (CB), H_2 (CA)
11. Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O. As an acid: $H_2O(aq) + NH_3(aq) \leftrightharpoons NH_4^+(aq) + OH^-(aq)$ As a base: H_{2}O\textit{(aq)} + HCl\textit{(aq)} \leftrightharpoons H_{3}O^{+}\textit{(aq)} + Cl^{-}\textit{(aq)}
12. amphiprotic: (a)
$$NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$$
$$NH_3 + OCH_3{}^- \longrightarrow NH_2{}^- + CH_3OH$$
(b)
$$HPO_4{}^{2-} + OH^- \longrightarrow PO_4{}^{3-} + H_2O$$
$$HPO_4{}^{2-} + HClO_4 \longrightarrow H_2PO_4{}^- + ClO_4{}^-$$
not amphiprotic: (c) Br^- (d) $NH_4{}^+$ (e) $AsO_4{}^{3-}$
13. (a) HCl, NaOH; (b) HCl, $Mg(OH)_2$; (c) H_2SO_4, NaOH; (d) HNO_3, NaOH; (e) H_3PO_4, KOH
14. $Na_2CO_3(s) + 2HBr(aq) \rightarrow 2NaBr(aq) + CO_2(g) + H_2O(l)$
15. acid + metal → hydrogen + ionic compound
16. $2HCl(aq) + Mg(s) \rightarrow H_2(g) + MgCl_2(aq)$
17. acid + metal oxide → salt + $H_2O(l)$
18. $2HNO_3(aq) + CuO(s) \rightarrow CuNO_3(aq) + 2H_2O(l)$
19. $$H_2O(l) + H_2O(l) \leftrightharpoons H_3O^+(aq) + OH^-(aq)$$
20. $[H^+] = 1.0 \times 10^{-9}$ *M*, solution is basic since $[OH^-] > [H^+]$
21. $[OH^-] = 5.0 \times 10^{-13}$ *M*, solution is acidic since $[H^+] > [OH^-]$
22. $[H^+] = 1.0 \times 10^{-7}$ *M*, the solution is neutral since $[H^+] = [OH^-]$
23. endothermic, temperature is going up from 40 to 60°C. Water absorbs heat on reactant side to shift to make more product (ionization of water). (View the video "14.14 | Is the self-ionization of water endothermic or exothermic?" for an explanation of this answer
24. In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C, $[H_3O\ ] = [OH^-] = (2.9 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}$.
25. In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C, $[H_3O\ ] = [OH^-] = (2.9 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}$. pH = pOH = $-\log[1.7 \times 10^{-7}\ M] = 6.77$
26. In a neutral solution $[H_3O^+] = [OH^-]$. At 60 °C, $[H_3O\ ] = [OH^-] = (9.311 \times 10^{-14})^{1/2} = 3.051 \times 10^{-7}$. The pH = pOH = $-\log[3.051 \times 10^{-7}\ M] = 6.5156$
27. (a) pH = 0.699, pOH = 13.301; (b) pOH = 1.845, pH = 12.155; (c) pH = -0.477; pOH = 15.477; (d) Here 0.0031 *M*

$Ca(OH)_2$ yields 2 $[OH^-]$ ions for every one molecule the base. So, $[OH^-] = 6.2 \times 10^{-3}$ and pOH = 2.21, pH = 11.79

28. (a) pH = 3.587; pOH = 10.413; (b) pOH = 0.68; pH = 13.32; (c) Here 0.000071 *M* $Ba(OH)_2$ yields 2 $[OH^-]$ ions for every one molecule the base. So, $[OH^-] = 1.42 \times 10^{-4}$ and pOH = 3.85, pH = 10.15 (d) pH = −0.40; pOH = 14.40
29. pH = -0.30, pOH = 14.30
30. $[H_3O^+] = 3.0 \times 10^{-7}$ *M*, $[OH^-] = 3.3 \times 10^{-8}$ *M*
31. $[H_3O^+] = 10^{-3.500} = 3.16 \times 10^{-4}$ *M*, $[OH^-] = 10^{-10.5} = 3.16 \times 10^{-11}$ *M*
32. $[H_3O^+] = 1 \times 10^{-2}M$; $[OH^-] = 1 \times 10^{-12}M$
33. $[OH^-] = 5.9 \times 10^{-9}$ *M*
34. $[H_3O^+] = 3.1 \times 10^{-12}$ *M*
35. $[OH^-] = 0.175$ *M*
36. [HCl] = 0.690 *M*
37. $[Ba(OH)_2] = 0.288$ *M*
38. $[H_2SO_4] = 0.151$ *M*
39. 20.8 mL of NaOH is needed to neutralize the acid.
40. (a) 11.9 mL of HNO_3 solution is needed to neutralize the base solution; (b) 9.72 mL of $Ba(OH)_2$ is needed to neutralize the acid solution
41. A buffer is the combination of a weak acid or base and a salt of that weak acid or base and they resist a change in pH upon dilution or upon the addition of small amounts of acid or base.
42. No, buffers cannot be made from a strong acid (or strong base) and its conjugate. This is because they both ionize completely.
43. (a) no; (b) yes; (c) no; (d) yes
44. 3b: when a strong acid is added: $NO_2^- + H^+ \rightarrow HNO_2$; when a strong base is added: $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$; 3d: strong base added: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$; strong acid: $NH_3 + H^+ \rightarrow NH_4^+$

CHAPTER 17: EQUILIBRIUM AND EQUILIBRIUM CONSTANTS

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

In this chapter, you will learn about

- Chemical reaction rates
- The dynamic nature of a chemical equilibrium
- Equilibrium constants
- The response of a stressed equilibrium using Le Châtelier’s Principle
- Equilibrium calculations involving changes to the equilibrium
- Equilibrium constants representing solubility, acids and bases
- Real world examples of equilibria in nature

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Chemical equations
- Reaction stoichiometry
- Molarity
- Solubility
- Reactions of acids and bases

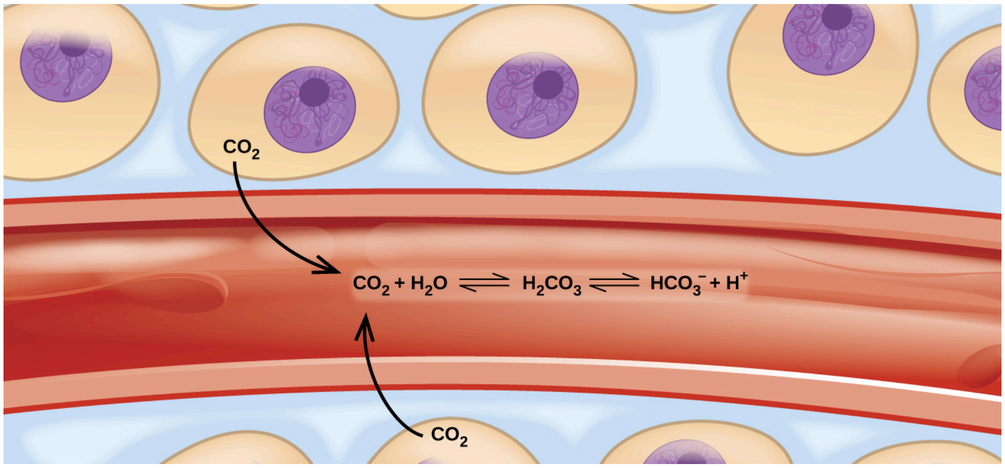

Figure 17a Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot and want to cool off, they head into the surf to swim. As the swimmers tire, they head to the beach to rest. If these two rates of transfer (sunbathers entering the water, swimmers leaving the water) are equal, the number of sunbathers and swimmers would be constant, or at equilibrium, although the identities of the people are constantly changing from sunbather to swimmer and back. An analogous situation occurs in chemical reactions. Reactions can occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance.

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (HCO_3^-) (Figure 17.a). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO_3^- and H^+). In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

Attribution & References

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17.1 CHEMICAL REACTION RATES

Learning Objectives

By the end of this section, you will be able to:

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A rate is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more coloured substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

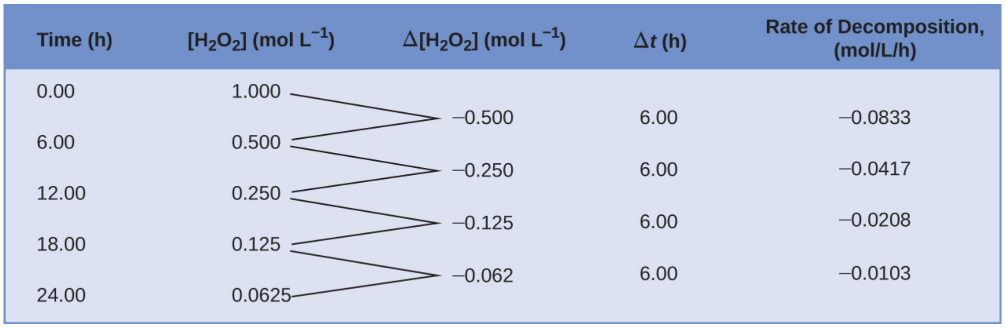
For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2\mathrm{H_2O_2}(aq) \longrightarrow 2\mathrm{H_2O}(l) + \mathrm{O_2}(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}}\\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1}\\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

This mathematical representation of the change in **species (chemical)** concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[H_2O_2]t_1$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]t_2$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure 17.1a provides an example of data collected during the decomposition of H_2O_2.



Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
		−0.500	6.00	−0.0833
6.00	0.500			
		−0.250	6.00	−0.0417
12.00	0.250			
		−0.125	6.00	−0.0208
18.00	0.125			
		−0.062	6.00	−0.0103
24.00	0.0625			

Figure 17.1a The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500 \text{ mol/L} - 1.000 \text{ mol/L})}{(6.00 \text{ h} - 0.00 \text{ h})} = 0.0833 \text{ mol L}^{-1}\text{h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625 \text{ mol/L} - 0.125 \text{ mol/L})}{(24.00 \text{ h} - 18.00 \text{ h})} = 0.0104 \text{ mol L}^{-1}\text{h}^{-1}$$

This behaviour indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 17.1b). We can use calculus to evaluate the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

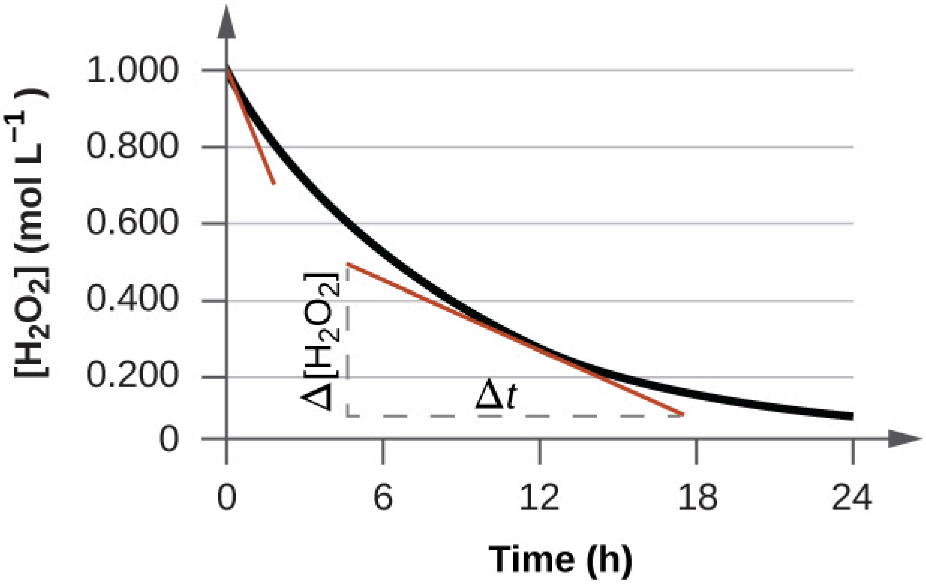


Figure 17.1b This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at $t = 0$ h ("initial rate") and at $t = 10$ h ("instantaneous rate" at that particular time) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 17.1c). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in colour upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$\mathrm{C_6H_{12}O_6} + \mathrm{O_2} \xrightarrow[\text{catalyst}]{} \mathrm{C_6H_{10}O_6} + \mathrm{H_2O_2}$$

$$2\mathrm{H_2O_2} + 2\mathrm{I^-} \xrightarrow[\text{catalyst}]{} \mathrm{I_2} + 2\mathrm{H_2O} + \mathrm{O_2}$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colourless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct colour change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis.* A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the colour-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the colour change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

Figure 17.1c Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: work by J3D3, CC BY-SA 3.0)

Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction. Consider the reaction represented by the following equation:

$$2NH_3(g) \longrightarrow N_2(g)\ +\ 3H_2(g)$$

The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to relate reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol NH}_3}{\Delta t} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2}\frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

$$-\frac{1}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t}=\frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 form during the time required for the formation of one mole of N_2:

$$\frac{1}{3}\frac{\Delta[\mathrm{H_2}]}{\Delta t}=\frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Figure 17.1d illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at t = 500 seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91\ \times\ 10^{-6}\ M/\mathrm{s}}{9.71\ \times\ 10^{-6}\ M/\mathrm{s}}\approx 3$$

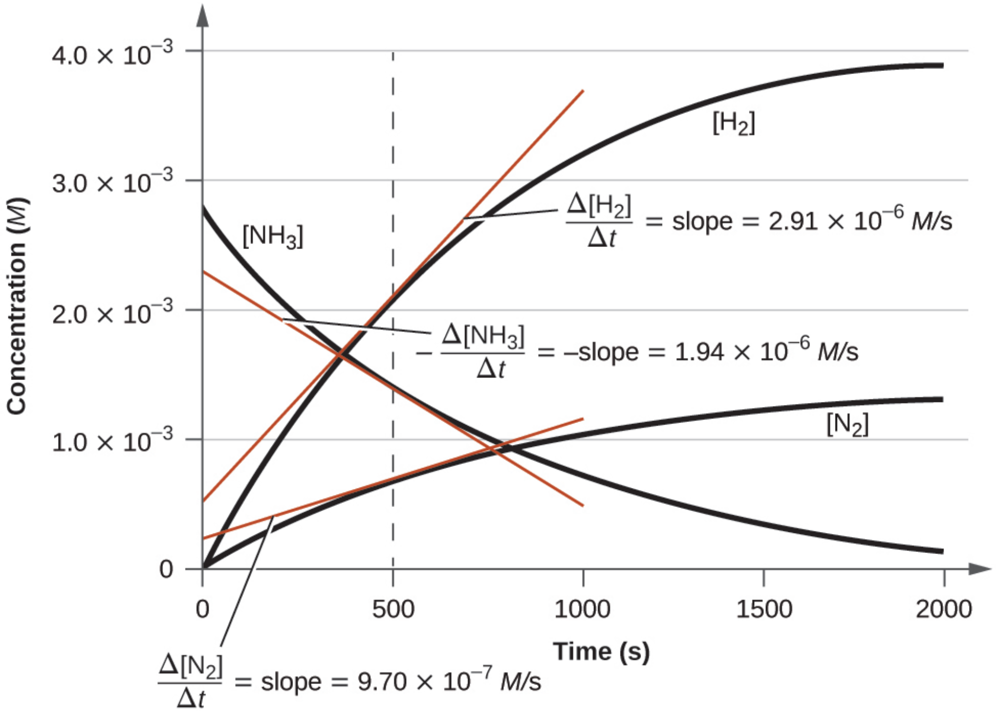


Figure 17.1d This graph shows the changes in concentrations of the reactants and products during the reaction $2NH_3$ → $3N_2$ + H_2. The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 17.1a

Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 17.1b shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20×10^{-2} mol/L/h, that is:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\ \text{mol L}^{-1}\text{h}^{-1}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

Using the stoichiometry of the reaction, we may determine that:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2}\ \text{mol L}^{-1}\text{h}^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2}\ \text{mol L}^{-1}\text{h}^{-1}$$

Exercise 17.1a

Check Your Learning Exercise (Text Version)

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10×10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

a. 5.30×10^{-6} mol/L/s, N_2 and 7.52×10^{-6} mol/L/s, H_2
b. 1.05×10^{-6} mol/L/s, N_2 and 3.15×10^{-6} mol/L/s, H_2

c. 3.15×10^{-6} mol/L/s, N_2 and 1.05×10^{-6} mol/L/s, H_2
d. 2.10×10^{-6} mol/L/s, N_2 and 6.30×10^{-6} mol/L/s, H_2

Check Your Answer[1]

Source: "Exercise 17.1a" is adapted from "Example 12.1-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Key Equations

- relative reaction rates for $aA \longrightarrow bB = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = \frac{1}{b}\frac{\Delta[B]}{\Delta t}$

Attribution & References

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Notes

1. b) 1.05×10^{-6} mol/L/s, N_2 and 3.15×10^{-6} mol/L/s, H_2

17.2 CHEMICAL EQUILIBRIA

Learning Objectives

By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical **equilibrium**, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colourless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

The colour becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Figure 17.2a).

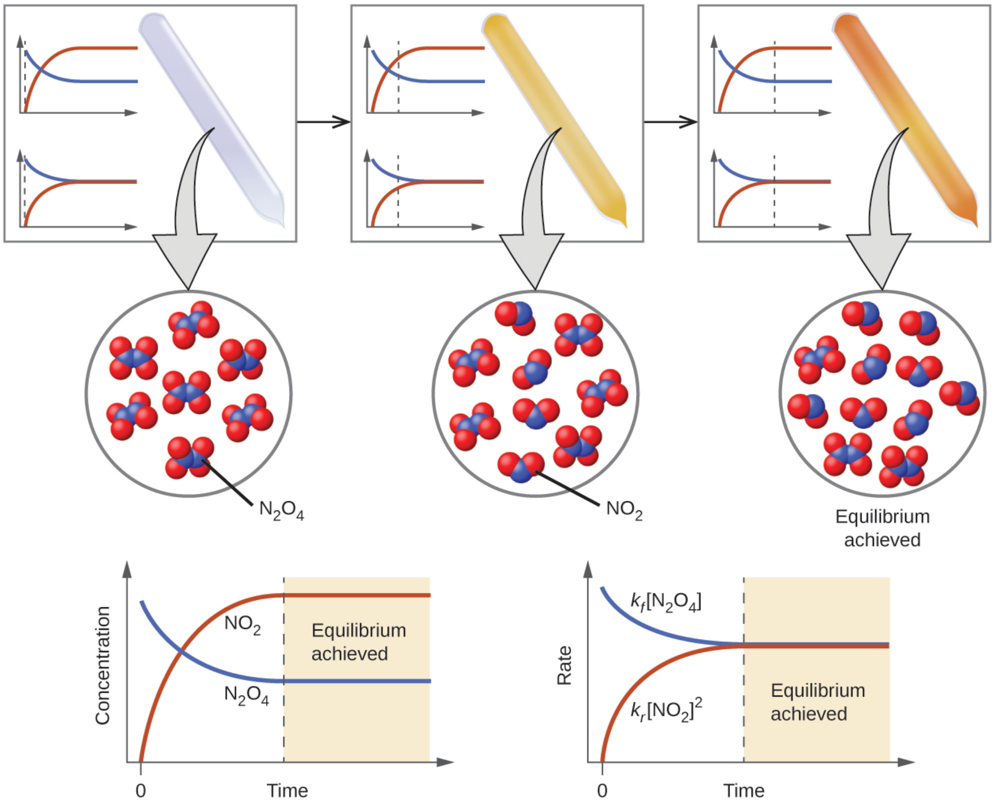

Figure 17.2a A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colourless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the colour of the mixture darkens due to the increasing concentration of NO_2 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The formation of NO_2 from N_2O_4 is a **reversible reaction**, which is identified by the equilibrium arrow ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure 17.2b).

Figure 17.2b These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant. (credit: work by Cmitasch, CC BY-SA 3.0)

Watch What is chemical equilibrium? (3 mins)

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 17.2a.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 17.2a shows the reaction:

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 17.2a, the rate of the forward reaction

$$2\mathrm{NO_2}(g) \longrightarrow \mathrm{N_2O_4}(g)$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4}(g) \longrightarrow 2\mathrm{NO_2}(g)$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled "Impregnating Water with Fixed Air." The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: "oil of vitriol" literally means "liquid nastiness") onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$\mathrm{H_2SO_4}(l)\ +\ \mathrm{CaCO_3}(s) \longrightarrow \mathrm{CO_2}(g)\ +\ \mathrm{H_2O}(l)\ +\ \mathrm{CaSO_4}(aq)$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions $(\mathrm{HCO_3}^-)$.

$$\mathrm{CO_2}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq)\ +\ \mathrm{H}^+(aq)$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles move up out of the beverage, releasing the gas into the air (Figure 17.2c). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."

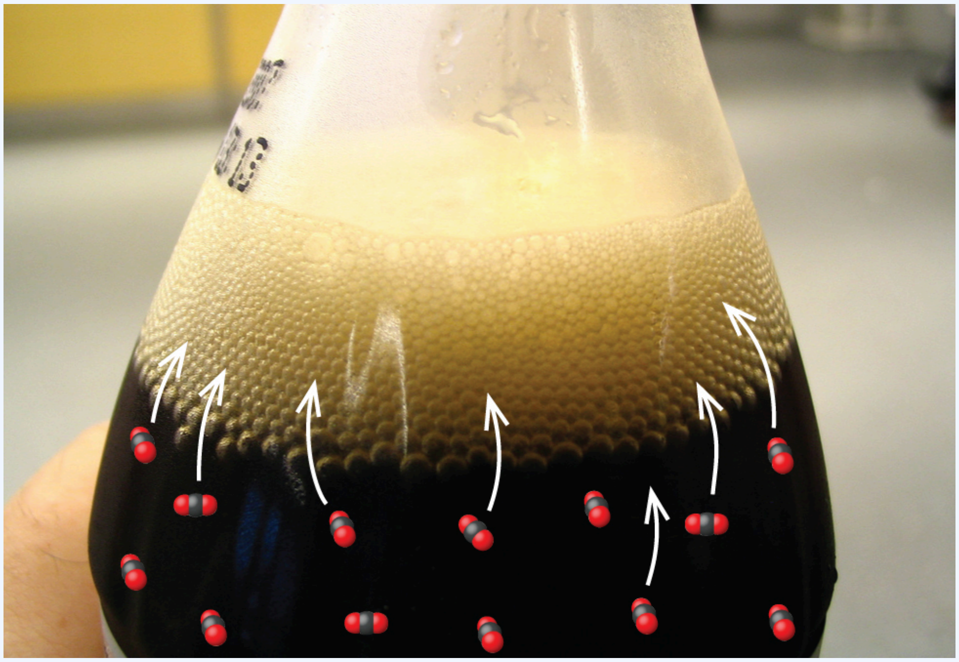

Figure 17.2c When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by Chiara Cotzee, PD; in *Chemistry (OpenStax)*, CC BY 4.0).

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure 17.2d shows a sample of liquid bromine at equilibrium with bromine vapour in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapour, some liquid evaporates, the amount of liquid decreases, and the amount of vapour increases. If we cap the bottle so no vapour escapes, the amount of liquid and vapour will eventually stop changing and an equilibrium between the liquid and the vapour will be established. If the bottle were not capped, the bromine vapour would escape and no equilibrium would be reached.

Figure 17.2d An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapour, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapour cannot escape and equilibrium is maintained. (credit: work by Anonymous/Images of Elements, CC BY 3.0)

Exercise 17.2a

Check Your Learning Exercise (Text Version)
True or False? If the concentrations of products and reactants are equal, the system is at equilibrium.

Check Your Answer[1]

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Links to Interactive Learning Tools

Explore Equilibrium Concept from the Physics Classroom.

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Notes

1. False. Equilibrium is reached when the forward and reverse reactions occur at equal rates. The concentrations of products and reactants remain constant.

17.3 EQUILIBRIUM CONSTANTS

Learning Objectives

By the end of this section, you will be able to:

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol ($\rightleftharpoons$) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$$

We can write the **reaction quotient (Q)** for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[\text{C}]^x[\text{D}]^y}{[\text{A}]^m[\text{B}]^n}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ is given by this expression:

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

Example 17.3a

Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3O_2(g) \rightleftharpoons 2O_3(g)$
b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
c. $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

Solution

a. $Q_c = \frac{[O_3]^2}{[O_2]^3}$
b. $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
c. $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Exercise 17.3a

Write the expression for the reaction quotient for each of the following reactions:

a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
b. $C_4H_8(g) \rightleftharpoons 2C_2H_4(g)$
c. $2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$

Check Your Answer[1]

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 17.3a). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

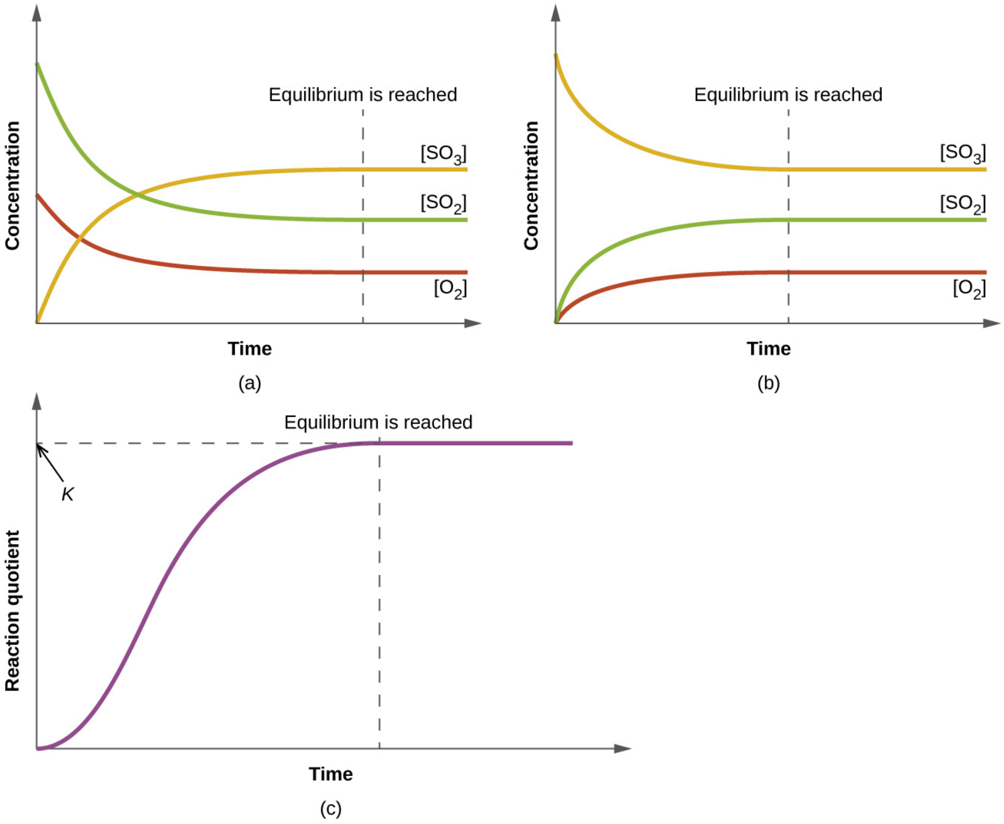

Figure 17.3a (a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the **equilibrium constant (*K*)** of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y\ldots}{[\mathrm{A}]^m[\mathrm{B}]^n\ldots}$$

This equation is a mathematical statement of the **law of mass action**: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example 17.3b

Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\mathrm{NO_2}(g) \rightleftharpoons \mathrm{N_2O_4}(g)$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[NO_2]$ = 0.016 *M* and $[N_2O_4]$ = 0.042 *M*.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

a. Before any product is formed, $[\mathrm{NO_2}] = \dfrac{0.10\ \mathrm{mol}}{1.0\ \mathrm{L}} = 0.10\ M$, and $[N_2O_4]$ = 0 *M*. Thus,

$$Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from concentrations instead of actual concentrations, and so K_c values are truly unitless.

Exercise 17.3b

Check Your Learning Exercise (Text Version)

For the reaction, $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$ the concentrations at equilibrium are $[SO_2]$ = 0.90 *M*, $[O_2]$ = 0.35 *M*, and $[SO_3]$ = 1.1 *M*. What is the value of the equilibrium constant, K_c?

a. 1.1
b. 4.3
c. 8.6
d. 0.90

Check Your Answer[2]

Source: "Exercise 17.3b" is adapted from "Example 13.2-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 17.3b illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$\mathrm{CO}(g) \ + \ \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) \ + \ \mathrm{H_2}(g) \qquad K_c = 0.640 \qquad \mathrm{T} = 800\ ^\circ\mathrm{C}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure 17.3b when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

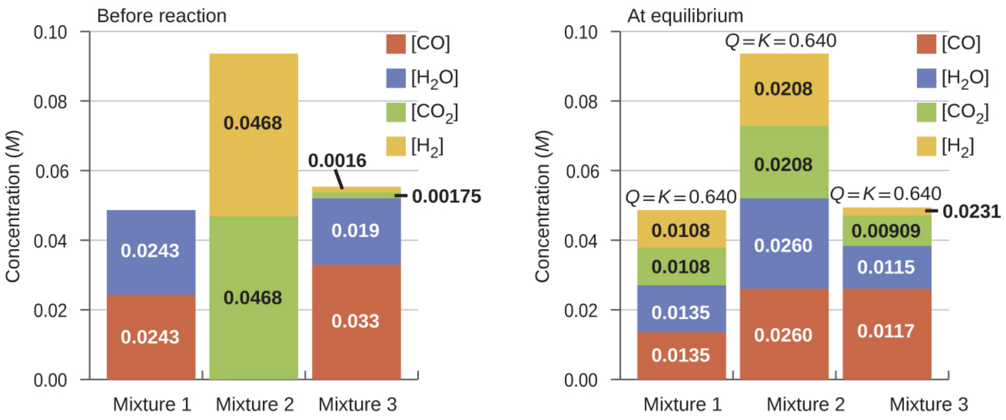

Figure 17.3b Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 17.3c

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO}(g) \ + \ \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) \ + \ \mathrm{H_2}(g)$$
$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.0203 M	0.011 M	0.0094 M
$[H_2O]_i$	0.0203 M	0.0011 M	0.0025 M
$[CO_2]_i$	0.0040 M	0.037 M	0.0015 M
$[H_2]_i$	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

$$Q_c = \frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

Exercise 17.3c

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

a. A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl2(g), and 0.500 mol of NOCl:
$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_c = 4.6 \times 10^4$$
b. A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.060$$
c. A 2.00-L flask containing 230 g of $SO_3(g)$:
$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_c = 0.230$$

Check Your Answer[3]

In Example 17.3c, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (unitless) quantities and are in essence "adjusted" concentrations.
- For relatively dilute solutions, a substance's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.

As a consequence of this last consideration, Q_c and K_c expressions do not contain terms for solids or liquids (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

Homogeneous Equilibria

A **homogeneous equilibrium** is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here.

$$\mathrm{C_2H_2}(aq) + 2\mathrm{Br_2}(aq) \rightleftharpoons \mathrm{C_2H_2Br_4}(aq) \quad K_c = \frac{[\mathrm{C_2H_2Br_4}]}{[\mathrm{C_2H_2}][\mathrm{Br_2}]^2}$$

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3}^-(aq) \quad K_c = \frac{[\mathrm{I_3}^-]}{[\mathrm{I_2}][\mathrm{I^-}]}$$

$$\mathrm{Hg_2}^{2+}(aq) + \mathrm{NO_3}^-(aq) + 3\mathrm{H_3O^+}(aq)$$

$$\rightleftharpoons 2\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + 4\mathrm{H_2O}(l) \quad K_c = \frac{[\mathrm{Hg^{2+}}]^2[\mathrm{HNO_2}]}{[\mathrm{Hg_2}^{2+}][\mathrm{NO_3}^-][\mathrm{H_3O^+}]^3}$$

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \quad K_c = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]}$$

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4}^+(aq) + \mathrm{OH^-}(aq) \quad K_c = \frac{[\mathrm{NH_4}^+][\mathrm{OH^-}]}{[\mathrm{NH_3}]}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, its concentration does not appear as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well.

$$\begin{aligned} C_2H_6(g) &\rightleftharpoons C_2H_4(g) + H_2(g) & K_c &= \frac{[C_2H_4][H_2]}{[C_2H_6]} \\ 3O_2(g) &\rightleftharpoons 2O_3(g) & K_c &= \frac{[O_3]^2}{[O_2]^3} \\ N_2(g) + 3H_2(g) &\rightleftharpoons 2NH_3(g) & K_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ C_3H_8(g) + 5O_2(g) &\rightleftharpoons 3CO_2(g) + 4H_2O(g) & K_c &= \frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5} \end{aligned}$$

Note that the concentration of $H_2O(g)$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

$$\begin{aligned} PV &= nRT \\ P &= \left(\tfrac{n}{V}\right) RT \\ &= MRT \end{aligned}$$

Thus, at constant temperature, the pressure of a gas is directly proportional to its concentration.

Using the partial pressures of the gases, we can write the reaction quotient for the system $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$ by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{C_2H_6}$ is the partial pressure of C_2H_6; P_{H_2}, the partial pressure of H_2; and $P_{C_2H_6}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}}$$

The subscript *P* in the symbol $\boldsymbol{K_P}$ designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for $\boldsymbol{K_c}$, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$:

$$\begin{aligned} K_P &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \\ &= \frac{([\text{C}] \times RT)^x ([\text{D}] \times RT)^y}{([\text{A}] \times RT)^m ([\text{B}] \times RT)^n} \\ &= \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \\ &= K_c (RT)^{(x+y) - (m+n)} \\ &= K_c (RT)^{\Delta n} \end{aligned}$$

The relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\text{A} + n\text{B} \leftrightharpoons x\text{C} + y\text{D}$, we have

$$\Delta n = (x + y) - (m + n)$$

Example 17.3d

Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:

a. $\text{C}_2\text{H}_6(g) \rightleftharpoons \text{C}_2\text{H}_4(g) + \text{H}_2(g)$
b. $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$
c. $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:
$\text{CS}_2(g) + 4\text{H}_2(g) \rightleftharpoons \text{CH}_4(g) + 2\text{H}_2\text{S}(g)$

What is K_P at this temperature?

Solution

a. $\Delta n = (2) - (1) = 1$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^1 = K_c\,(RT)$

b. $\Delta n = (2) - (2) = 0$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^0 = K_c$

c. $\Delta n = (2) - (1 + 3) = -2$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{-2} = \dfrac{K_c}{(RT)^2}$

d. $K_P = K_c\,(\mathrm{RT})^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

Exercise 17.3d

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

a. $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{SO_3}(g)$
b. $\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$
c. $\mathrm{C_3H_8}(g) + 5\mathrm{O_2}(g) \rightleftharpoons 3\mathrm{CO_2}(g) + 4\mathrm{H_2O}(g)$
d. At 227 °C, the following reaction has $K_c = 0.0952$:
$\mathrm{CH_3OH}(g) \rightleftharpoons \mathrm{CO}(g) + 2\mathrm{H_2}(g)$
What would be the value of K_P at this temperature

Check Your Answer[4]

Heterogeneous Equilibria

A **heterogeneous equilibrium** is a system in which reactants and products are found in two or more phases.

The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes; for example:

$$\begin{aligned} \mathrm{PbCl_2}(s) &\rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\mathrm{Cl^-}(aq) & K_c &= [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \\ \mathrm{CaO}(s) + \mathrm{CO_2}(g) &\rightleftharpoons \mathrm{CaCO_3}(s) & K_c &= \frac{1}{[\mathrm{CO_2}]} \\ \mathrm{C}(s) + 2\mathrm{S}(g) &\rightleftharpoons \mathrm{CS_2}(g) & K_c &= \frac{[\mathrm{CS_2}]}{[\mathrm{S}]^2} \end{aligned}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$\mathrm{Br_2}(l) \rightleftharpoons \mathrm{Br_2}(g) \qquad K_c = [\mathrm{Br_2}]$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using partial pressures instead of concentrations. Two examples are:

$$\begin{aligned} \mathrm{CaO}(s) + \mathrm{CO_2}(g) &\rightleftharpoons \mathrm{CaCO_3}(s) & K_P &= \frac{1}{P_{\mathrm{CO_2}}} \\ \mathrm{C}(s) + 2\mathrm{S}(g) &\rightleftharpoons \mathrm{CS_2}(g) & K_P &= \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \end{aligned}$$

Links to Interactive Learning Tools

Explore Equilibrium Constant Expression from the Physics Classroom.

Key Equations

- $Q = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \quad \text{where } m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n} \quad \text{where } m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_\mathrm{P} = K_\mathrm{c}(RT)^{\Delta n}$

Attribution & References

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Notes

1. (a) $Q_c = \frac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2[\mathrm{O_2}]}$; (b) $Q_c = \frac{[\mathrm{C_2H_4}]^2}{[\mathrm{C_4H_8}]}$; (c) $Q_c = \frac{[\mathrm{CO_2}]^8[\mathrm{H_2O}]^{10}}{[\mathrm{C_4H_{10}}]^2[\mathrm{O_2}]^{13}}$
2. b) 4.3
3. (a) $Q_c = 6.45 \times 10^3$, shifts right. (b) $Q_c = 0.12$, shifts left. (c) $Q_c = 0$, shifts right
4.
    1. $K_P = K_c(RT)^{-1}$;
    2. $K_P = K_c(RT)$;
    3. $K_P = K_c(RT)$;
    4. 160 or 1.6×10^2

17.4 SHIFTING EQUILIBRIA: LE CHÂTELIER'S PRINCIPLE

Learning Objectives

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). Next we address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or **stress** (such as a change in concentration) the **position of equilibrium** changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < \mathrm{K}$) or the reactants (if $\mathrm{Q} > K$) until Q returns to the same value as K.

This process is described by **Le Châtelier's principle**: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Châtelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

Effect of Change in Concentration on Equilibrium

A chemical system at equilibrium can be temporarily shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure 17.4a is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Châtelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.

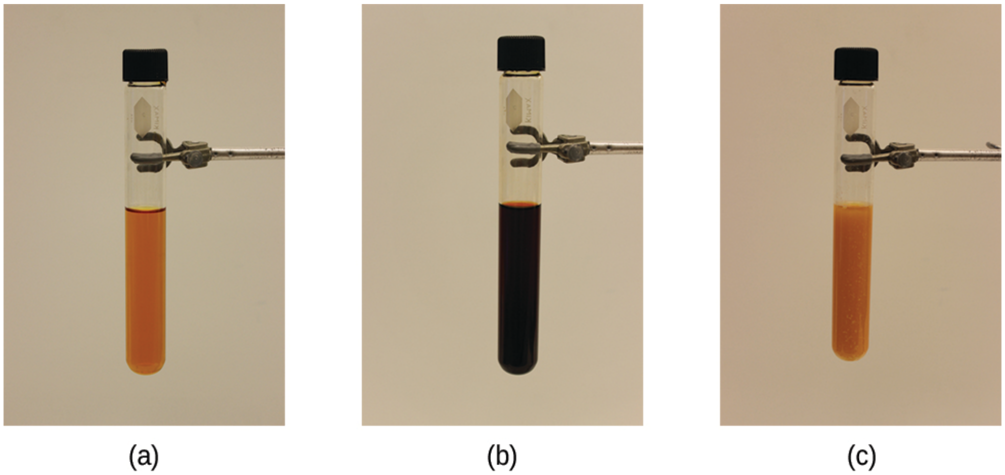

Figure 17.4a (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN^- as the white solid AgSCN. $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN^- concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening colour) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \qquad K_c = 50.0 \text{ at } 400\ ^\circ\text{C}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which $[H_2] = 0.374\ M$, $[I_2] = 0.153\ M$, and $[HI] = 1.692\ M$. This gives:

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

Check out this video to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

Watch **Volume Effect on Equilibrium – LeChatelier's Principle Lab Extension (0:43 min)**

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Châtelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favoured because this relieves the stress. The reverse reaction would be favoured by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\mathrm{NO}(g)\ +\ \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favours decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$\mathrm{N_2}(g)\ +\ \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO}(g)$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favour either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Châtelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$\mathrm{H_2}(g) \ + \ \mathrm{I_2}(g) \rightleftharpoons \mathrm{2HI}(g) \qquad \Delta H = -9.4 \text{ kJ (exothermic)}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2}(g) \ + \ \mathrm{I_2}(g) \rightleftharpoons \mathrm{2HI}(g) \ + \ \text{heat}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favours the production of heat, and favours the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$\mathrm{N_2O_4}(g) \rightleftharpoons \mathrm{2NO_2}(g) \qquad \Delta H = 57.20 \text{ kJ}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} \ + \ \mathrm{N_2O_4}(g) \rightleftharpoons \mathrm{2NO_2}(g)$$

At higher temperatures, the gas mixture has a deep brown colour, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colourless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown colour to fade.

Table 17.4a Effects of Disturbances of Equilibrium and g

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year.

Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibres, and is also used in the steel industry.

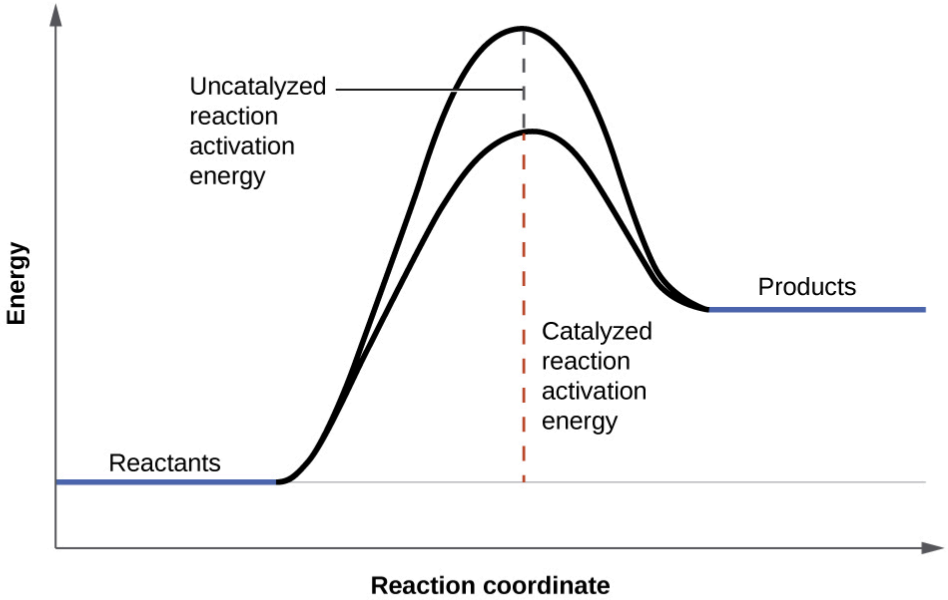

Figure 17.4b The presence of a catalyst increases the rate of a reaction by lowering its activation energy (*General Chemistry 1 & 2*, CC BY 4.0).

Fritz Haber

Figure 17.4c The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery. (credit: work by The Nobel Foundation, PD)

In the early 20th century, German chemist Fritz Haber (Figure 17.4c) developed a practical process for converting diatomic nitrogen, which cannot be used by plants as a nutrient, to ammonia, a form of nitrogen that is easiest for plants to absorb.

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$$

The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate. Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, "During peace time a scientist belongs to the World, but during war time he belongs to his country."[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

Indigenous Perspective: The Three Sisters

Also in relation to nitrogen-fixation, a number of Indigenous communities have used another method for nitrogen fixation for hundreds of years. Termed "The Three Sisters", corn, squash and beans are co-planted, and their symbiotic relationship allows for all three plants to produce optimum yields. The corn stalks provide support, giving the bean plants a vertical space to grow upwards. The squash plant's large leaves help maintain soil moisture and can prevent weeds. The bean plants are a natural source of nitrogen-fixation, which helps supports all of the plants. Briefly, the bean plants host the microbe, *rhizobia*, that converts nitrogen from the air into ammonia. This ammonia can then be absorbed by the plant roots.

To learn more about the Three Sisters, **Watch** **Three Sisters: Companion Planting of North American Indigenous Peoples (10:54 min)**:

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$\mathrm{N_2}(g) \ + \ 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$\mathrm{N_2}(g) \ + \ 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g) \qquad \Delta H = -92.2 \text{ kJ}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favour the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure 17.4d).

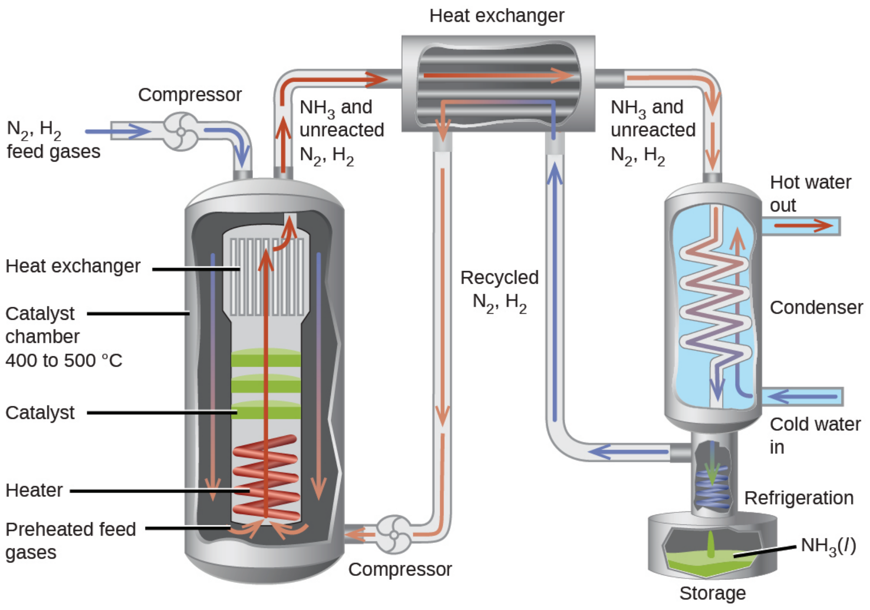

Figure 17.4d Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 17.4a

Check Your Learning Exercise (Text Version)

Based on the following chemical equation, how can you increase the equilibrium concentration of hydrazine, N_2H_4?

$N_{2(g)} + 2H_{2(g)} \leftrightarrow N_2H_{4(g)}$ $\Delta H = 95$ kJ

a. Add more N_2

b. Add more H_2
c. Increase temperature
d. All of the above

Check Your Answer[2]

Source: "Exercise 17.4a" is adapted from "Exercise 13.3-7" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Links to Interactive Learning Tools

Explore LeChatelier's Principle from the Physics Classroom.

Attribution & References

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Notes

1. Herrlich, P. "The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?" *EMBO Reports* 14 (2013): 759–764.
2. d) All of the above

17.5 EQUILIBRIUM CALCULATIONS

Learning Objectives

By the end of this section, you will be able to:

- Write equations representing changes in concentration and pressure for chemical species in equilibrium systems
- Use algebra to perform various types of equilibrium calculations

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for Q to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

$$2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) \;+\; 3\text{H}_2(g)$$

If a sample of ammonia decomposes in a closed system and the concentration of N_2 increases by 0.11 M, the change in the N_2 concentration, $\Delta[N_2]$, the final concentration minus the initial concentration, is 0.11 M. The change is positive because the concentration of N_2 increases.

The change in the H_2 concentration, $\Delta[H_2]$, is also positive—the concentration of H_2 increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of H_2 is three times the change in the concentration of N_2 because for each mole of N_2 produced, 3 moles of H_2 are produced.

$$\Delta[\text{H}_2] = 3 \;\times\; \Delta[\text{N}_2]$$

$$= 3 \times (0.11\ M) = 0.33\ M$$

The change in concentration of NH_3, $\Delta[NH_3]$, is twice that of $\Delta[N_2]$; the equation indicates that 2 moles of NH_3 must decompose for each mole of N_2 formed. However, the change in the NH_3 concentration is negative because the concentration of ammonia *decreases* as it decomposes.

$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2 \times (0.11\ M) = -0.22\ M$$

We can relate these relationships directly to the coefficients in the equation:

$$\begin{array}{ccccc} 2\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\mathrm{H_2}(g) \\ \Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] & & \Delta[\mathrm{N_2}] = 0.11\ M & & \Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] \end{array}$$

Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of N_2, we could represent it by the symbol x.

$$\Delta[\mathrm{N_2}] = x$$

The changes in the other concentrations would then be represented as:

$$\Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] = 3x$$
$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$$\begin{array}{ccccc} 2\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\mathrm{H_2}(g) \\ -2x & & x & & 3x \end{array}$$

The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example 17.5a

Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

a. $$\begin{array}{lllllll} C_2H_2(g) & + & 2Br_2(g) & \rightleftharpoons & C_2H_2Br_4(g) \\ x & & \_\_\_\_\_\_ & & \_\_\_\_\_\_ \end{array}$$

b. $$\begin{array}{lllllll} I_2(aq) & + & I^-(aq) & \rightleftharpoons & {I_3}^-(aq) \\ \_\_\_\_\_\_ & & \_\_\_\_\_\_ & & x \end{array}$$

c. $$\begin{array}{lllllllll} C_3H_8(g) & + & 5O_2(g) & \rightleftharpoons & 3CO_2(g) & + & 4H_2O(g) \\ x & & \_\_\_\_\_\_ & & \_\_\_\_\_\_ & & \_\_\_\_\_\_ \end{array}$$

Solution

a. $$\begin{array}{lllllll} C_2H_2(g) & + & 2Br_2(g) & \rightleftharpoons & C_2H_2Br_4(g) \\ x & & 2x & & -x \end{array}$$

b. $$\begin{array}{lllllll} I_2(aq) & + & I^-(aq) & \rightleftharpoons & {I_3}^-(aq) \\ -x & & -x & & x \end{array}$$

c. $$\begin{array}{lllllllll} C_3H_8(g) & + & 5O_2(g) & \rightleftharpoons & 3CO_2(g) & + & 4H_2O(g) \\ x & & 5x & & -3x & & -4x \end{array}$$

Exercise 17.5a

Complete the changes in concentrations for each of the following reactions:

a. $$\begin{array}{ccccc} 2\mathrm{SO_2}(g) & + & \mathrm{O_2}(g) & \rightleftharpoons & 2\mathrm{SO_3}(g) \\ \underline{\hspace{1.5cm}} & & x & & \underline{\hspace{1.5cm}} \end{array}$$

b. $$\begin{array}{ccc} \mathrm{C_4H_8}(g) & \rightleftharpoons & 2\mathrm{C_2H_4}(g) \\ \underline{\hspace{1.5cm}} & & -2x \end{array}$$

c. $$\begin{array}{ccccccc} 4\mathrm{NH_3}(g) & + & 7\mathrm{H_2O}(g) & \rightleftharpoons & 4\mathrm{NO_2}(g) & + & 6\mathrm{H_2O}(g) \\ \underline{\hspace{1.5cm}} & & \underline{\hspace{1.5cm}} & & \underline{\hspace{1.5cm}} & & \underline{\hspace{1.5cm}} \end{array}$$

Check Your Answer[1]

Calculations Involving Equilibrium Concentrations

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q_c (i.e., *the law of mass action*) to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q_c = K_c$ (at equilibrium) in all of these situations and that there are only three basic types of calculations:

1. **Calculation of an equilibrium constant**. If concentrations of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. **Calculation of missing equilibrium concentrations**. If the value of the equilibrium constant and all of the equilibrium concentrations, except one, are known, the remaining concentration can be calculated.
3. **Calculation of equilibrium concentrations from initial concentrations**. If the value of the equilibrium constant and a set of concentrations of reactants and products that are not at equilibrium are known, the concentrations at equilibrium can be calculated.

A similar list could be generated using Q_P, K_P, and partial pressure. We will look at solving each of these cases in sequence.

Calculation of an Equilibrium Constant

Since the law of mass action is the only equation we have to describe the relationship between K_c and the concentrations of reactants and products, any problem that requires us to solve for K_c must provide enough information to determine the reactant and product concentrations at equilibrium. Armed with the concentrations, we can solve the equation for K_c, as it will be the only unknown.

The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE chart—for **I**nitial, **C**hange, and **E**quilibrium–will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. Underneath the reaction the initial concentrations of the reactants and products are listed—these conditions are usually provided in the problem and we consider no shift toward equilibrium to have happened. The next row of data is the change that occurs as the system shifts toward equilibrium—do not forget to consider the reaction stoichiometry as described in a previous section of this chapter. The last row contains the concentrations once equilibrium has been reached.

Example 17.5b

Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$\mathrm{I_2}(aq)\ +\ \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3}^-(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of I_2.

	I_2 +	I^- $\rightleftharpoons$	I_3^-
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x$	$-x$	$+x$
Equilibrium concentration (*M*)	$[1.000 \times 10^{-3}]_i - x$	$[1.000 \times 10^{-3}]_i - x$	x

Since the equilibrium concentration of I_2 is given, we can solve for *x*. At equilibrium the concentration of I_2 is 6.61×10^{-4} *M* so that

$$\begin{aligned} 1.000 \times 10^{-3} - x &= 6.61 \times 10^{-4} \\ x &= 1.000 \times 10^{-3} - 6.61 \times 10^{-4} \\ &= 3.39 \times 10^{-4}\ M \end{aligned}$$

Now we can fill in the table with the concentrations at equilibrium.

	I_2 +	I^- $\rightleftharpoons$	I_3^-
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x = -3.39 \times 10^{-4}$	$-x$	$+x$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

We now calculate the value of the equilibrium constant.

$$K_c = Q_c = \frac{[I_3{}^-]}{[I_2][I^-]}$$

$$= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776$$

Exercise 17.5b

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odour of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when 0.31 mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Check Your Answer[2]

Calculation of a Missing Equilibrium Concentration

If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

Example 17.5c

Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Find the concentration of NO(g) in an equilibrium mixture with air at 1 atm pressure at this temperature. In air, $[N_2]$ = 0.036 mol/L and $[O_2]$ 0.0089 mol/L.

Solution

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_c = Q_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$[NO]^2 = K_c[N_2][O_2]$$

$$[NO] = \sqrt{K_c[N_2][O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient to see whether it is equal to the equilibrium constant.

$$Q_c = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}$$
$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$
$$Q_c = 4.0 \times 10^{-4} = K_c$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

Exercise 17.5c

Check Your Learning Exercise (Text Version)
The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

a. 4.26 mol/L
b. 2.09 mol/L
c. 5.45 mol/L
d. 1.53 mol/L

Check Your Answer[3]

Source: “Exercise 17.5c” is adapted from “Example 13.4-3” in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Calculation of Changes in Concentration

If we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
    a. Write a balanced chemical equation for the reaction.
    b. If the direction in which the reaction must proceed to reach equilibrium is not obvious, calculate Q_c from the initial concentrations and compare to K_c to determine the direction of change.
2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
    a. Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol x and express the other changes in terms of the smallest change.
    b. Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
    a. Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for x, and check any assumptions used to find x.
    b. Calculate the equilibrium concentrations.
4. Check the arithmetic.
    a. Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant.

Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps.

In solving equilibrium problems that involve changes in concentration, sometimes it is convenient to set up an ICE table, as described in the previous section.

Example 17.5d

Calculation of Concentration Changes as a Reaction Goes to Equilibrium

Under certain conditions, the equilibrium constant for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 if the initial concentration of PCl_5 was 1.00 M?

Solution

Use the stepwise process described earlier.

1. *Determine the direction the reaction proceeds.*
   The balanced equation for the decomposition of PCl_5 is
   $$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g)$$
   Because we have no products initially, $Q_c = 0$ and the reaction will proceed to the right.
2. *Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.*
   Let us represent the increase in concentration of PCl_3 by the symbol x. The other changes may be written in terms of x by considering the coefficients in the chemical equation.
   $$\begin{array}{ccccc} \mathrm{PCl_5}(g) & \rightleftharpoons & \mathrm{PCl_3}(g) & + & \mathrm{Cl_2}(g) \\ -x & & x & & x \end{array}$$
   The changes in concentration and the expressions for the equilibrium concentrations are:

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	$0 + x = x$	$0 + x = x$

3. *Solve for the change and the equilibrium concentrations.*
   Substituting the equilibrium concentrations into the equilibrium constant equation gives
   $$\begin{aligned} K_c &= \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = 0.0211 \\ &= \frac{(x)(x)}{(1.00 - x)} \end{aligned}$$
   This equation contains only one variable, x, the change in concentration. We can write the equation as a quadratic equation and solve for x using the quadratic formula.
   $$\begin{aligned} 0.0211 &= \frac{(x)(x)}{(1.00 - x)} \\ 0.0211(1.00 - x) &= x^2 \\ x^2 + 0.0211x - 0.0211 &= 0 \end{aligned}$$

An equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for a, b, and c yields:

$$\begin{aligned} x &= \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)} \\ &= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2} \\ &= \frac{-0.0211 \pm 0.291}{2} \end{aligned}$$

Hence

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

or

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

Quadratic equations often have two different solutions, one that is physically possible and one that is physically impossible (an extraneous root). In this case, the second solution (−0.156) is physically impossible because we know the change must be a positive number (otherwise we would end up with negative values for concentrations of the products). Thus, $x = 0.135\ M$.

The equilibrium concentrations are

$$\begin{aligned} [\mathrm{PCl_5}] &= 1.00 - 0.135 = 0.87\ M \\ [\mathrm{PCl_3}] &= x = 0.135\ M \\ [\mathrm{Cl_2}] &= x = 0.135\ M \end{aligned}$$

4. *Check the arithmetic.*
   Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures). Thus, the calculated equilibrium concentrations check.

Exercise 17.5d

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$\mathrm{CH_3CO_2H} + \mathrm{C_2H_5OH} \rightleftharpoons \mathrm{CH_3CO_2C_2H_5} + \mathrm{H_2O}$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations when a mixture that is 0.15 *M* in CH_3CO_2H, 0.15 *M* in C_2H_5OH, 0.40 *M* in $CH_3CO_2C_2H_5$, and 0.40 *M* in H_2O are mixed in enough dioxane to make 1.0 L of solution?

Check Your Answer[4]

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products.

Consider the ionization of 0.150 M HA, a weak acid.

$$\mathrm{HA}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{A}^-(aq) \qquad K_c = 6.80 \times 10^{-4}$$

The most obvious way to determine the equilibrium concentrations would be to start with only reactants. This could be called the "all reactant" starting point. Using *x* for the amount of acid ionized at equilibrium, this is the ICE table and solution.

	$\mathrm{HA}(aq) \rightleftharpoons$	$\mathrm{H}^+(aq)$ +	$\mathrm{A}^-(aq)$
Initial concentration (*M*)	0.150	0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.150 - x$	x	x

Setting up and solving the quadratic equation gives

$$K_c = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} = \frac{(x)(x)}{(0.150 - x)} = 6.80 \times 10^{-4}$$

$$x^2 + (6.80 \times 10^{-4}x) - (1.02 \times 10^{-4}) = 0$$

$$x = \frac{-6.80 \times 10^{-4} \pm \sqrt{(6.80 \times 10^{-4})^2 - (4)(1)(-1.02 \times 10^{-4})}}{(2)(1)}$$

$$x = 0.00977\ M \text{ or } -0.0104\ M$$

Using the positive (physical) root, the equilibrium concentrations are

$$[\text{HA}] = 0.150 - x = 0.140\ M$$
$$[\text{H}^+] = [\text{A}^-] = x = 0.00977\ M$$

A less obvious way to solve the problem would be to assume all the HA ionizes first, then the system comes to equilibrium. This could be called the “all product” starting point. Assuming all of the HA ionizes gives

$$[\text{HA}] = 0.150 - 0.150 = 0\ M$$
$$[\text{H}^+] = 0 + 0.150 = 0.150\ M$$
$$[\text{A}^-] = 0 + 0.150 = 0.150\ M$$

Using these as initial concentrations and “*y*” to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

	$\text{HA}(aq)$ ⇌	$\text{H}^+(aq)$ +	$\text{A}^-(aq)$
Initial concentration (*M*)	0	0.150	0.150
Change (*M*)	$+y$	$-y$	$-y$
Equilibrium concentration (*M*)	y	$0.150 - y$	$0.150 - y$

Setting up and solving the quadratic equation gives

$$K_c = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.150 - y)(0.150 - y)}{(y)} = 6.80 \times 10^{-4}$$
$$6.80 \times 10^{-4} y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

$$y^2 - 0.30068y + 0.022500 = 0$$
$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)(0.022500)}}{(2)(1)}$$
$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

$$y = 0.160\ M \qquad \text{or} \qquad y = 0.140\ M$$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

$$[\text{HA}] = y = 0.140\ M$$

$$[\mathrm{H}^+] = 0.150 \; - \; y = 0.010 \; M$$
$$[\mathrm{A}^-] = 0.150 \; - \; y = 0.010 \; M$$

Thus, the two approaches give the same results (to three decimal places), and show that both starting points lead to the same equilibrium conditions. The "all reactant" starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the "all product" starting point had a relatively large change (y) that was nearly the size of the initial concentrations. It can be said that a system that starts "close" to equilibrium will require only a "small" change in conditions (x) to reach equilibrium.

Recall that a small K_c means that very little of the reactants form products and a large K_c means that most of the reactants form products. If the system can be arranged so it starts "close" to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%. The following two examples demonstrate this.

Example 17.5e

Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 *M* solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H}^+(aq) \; + \; \mathrm{CN}^-(aq) \qquad K_c = 4.9 \; \times \; 10^{-10}$$

Solution

Using "x" to represent the concentration of each product at equilibrium gives this ICE table.

	$\mathrm{HCN}(aq) \rightleftharpoons$	$\mathrm{H}^+(aq)$ +	$\mathrm{CN}^-(aq)$
Initial concentration (*M*)	0.15	0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.15 - x$	x	x

The exact solution may be obtained by solving for x in

$$K_c = 4.9 \; \times \; 10^{-10} = \frac{(x)(x)}{0.15 \; - \; x}$$

which, once multiplied through and rearranged, becomes

$$x^2 \; + \; 4.9 \; \times \; 10^{-10} \; - \; 7.35 \; \times \; 10^{-11} = 0$$

Using the quadratic formula with the above, x is determined to be

$$x = 8.5\underline{6} \times 10^{-6}\ M = 8.6 \times 10^{-6}\ M$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6} M$ and $[HCN] = 0.15 - x = 0.15\ M$.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, *x* must be small compared to 0.15 *M*. More formally, if $x \ll 0.15$, then $0.15 - x \approx 0.15$. If this assumption is true, then it simplifies obtaining *x*

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF $(0.15 - x) \approx 0.15\ M$, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\%$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

The second example requires that the original information be processed a bit, but it still can be solved using a small *x* approximation.

Example 17.5f

Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) \qquad K_c = 5.0 \times 10^{13}$$

$$K_c = \frac{[\text{Cu(NH}_3)_4{}^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 *M* NH_3 what are the concentrations when the system comes to equilibrium?

Solution

The initial concentration of copper(II) is 0.010 *M*. The equilibrium constant is very large so it would be better to start with as much product as possible because “all products” is much closer to equilibrium than “all reactants.” Note that Cu^{2+} is the limiting reactant; if all 0.010 *M* of it reacts to form product the concentrations would be

$$[\text{Cu}^{2+}] = 0.010 - 0.010 = 0\ M$$
$$[\text{Cu(NH}_3)_4{}^{2+}] = 0.010\ M$$
$$[\text{NH}_3] = 1.00 - 4 \times 0.010 = 0.96\ M$$

Using these “shifted” values as initial concentrations with *x* as the free copper(II) ion concentration at equilibrium gives this ICE table.

	$Cu^{2+}(aq)$ +	$4NH_3(aq)$ $\rightleftharpoons$	$Cu(NH_3)_4{}^{2+}(aq)$
Initial concentration (*M*)	0	0.96	0.010
Change (*M*)	$+x$	$+4x$	$-x$
Equilibrium concentration (*M*)	x	$0.96 + 4x$	$0.010 - x$

Since we are starting close to equilibrium, *x* should be small so that

$$0.96 + 4x \approx 0.96\ M$$
$$0.010 - x \approx 0.010\ M$$
$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$
$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[\mathrm{Cu}^{2+}] = x = 2.4 \times 10^{-16}\ M$$
$$[\mathrm{NH_3}] = 0.96 - 4x = 0.96\ M$$
$$[\mathrm{Cu(NH_3)_4}^{2+}] = 0.010 - x = 0.010\ M$$

By starting with the maximum amount of product, this system was near equilibrium and the change (*x*) was very small. With only a small change required to get to equilibrium, the equation for *x* was greatly simplified and gave a valid result well within the 5% error maximum.

Exercise 17.5e

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 *M* NH_3 solution?

$$\mathrm{Ni}^{2+}(aq) + 6\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ni(NH_3)_6}^{2+}(aq) \qquad K_c = 5.5 \times 10^8$$

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (*x*) of the product shifts left. Calculate the error in your assumption.

Check Your Answer[5]

Link to Interactive Learning Tools

Explore Equilibrium Calculations from the Physics Classroom.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "13.4 Equilibrium Calculations" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*

Notes

1. (a) $2x$, x, $-2x$; (b) x, $-2x$; (c) $4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$
2. $K_c = 5$
3. d) 1.53 mol/L
4. $[CH_3CO_2H] = 0.36\ M$, $[C_2H_5OH] = 0.36\ M$, $[CH_3CO_2C_2H_5] = 0.17\ M$, $[H_2O] = 0.17\ M$
5. $[Ni(NH_3)_6{}^{2+}] = 0.25\ M$, $[NH_3] = 0.50\ M$, $[Ni^{2+}] = 2.9 \times 10^{-8} M$, error $= 1.2 \times 10^{-5}\%$

17.6 PRECIPITATION AND DISSOLUTION

Learning Objectives

By the end of this section, you will be able to:

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

The preservation of medical laboratory blood samples, mining of sea water for magnesium, formulation of over-the-counter medicines such as Milk of Magnesia and antacids, and treating the presence of hard water in your home's water supply are just a few of the many tasks that involve controlling the equilibrium between a slightly soluble ionic solid and an aqueous solution of its ions.

In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula $Ca_5(PO_4)_3(OH)$, in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the CO_3^{2-} ions produced in this process help soothe an upset stomach.

In this section, we will find out how we can control the dissolution of a slightly soluble ionic solid by the application of Le Châtelier's principle. We will also learn how to use the equilibrium constant of the reaction to determine the concentration of ions present in a solution.

The Solubility Product Constant

Silver chloride is what's known as a sparingly soluble ionic solid (Figure 17.6a). Recall from the solubility rules in an earlier chapter that halides of Ag^+ are not normally soluble. However, when we add an excess of solid AgCl to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride:

$$\text{AgCl}(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

This equilibrium, like other equilibria, is dynamic; some of the solid AgCl continues to dissolve, but at the same time, Ag^+ and Cl^- ions in the solution combine to produce an equal amount of the solid. At equilibrium, the opposing processes have equal rates.

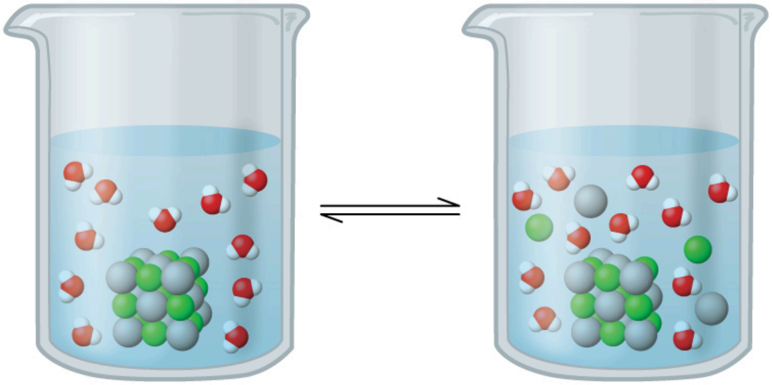


Figure 17.6a Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is called the **solubility product (K_{sp})** of the solid. Recall from the chapter on solutions and colloids that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \qquad K_{\text{sp}} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)]$$

When looking at dissolution reactions such as this, the solid is listed as a reactant, whereas the ions are listed as products. The solubility product constant, as with every equilibrium constant expression, is written as the product of the concentrations of each of the ions, raised to the power of their stoichiometric coefficients. Here, the solubility product constant is equal to Ag^+ and Cl^- when a solution of silver chloride is in equilibrium with undissolved AgCl. There is no denominator representing the reactants in this equilibrium expression since the reactant is a pure solid; therefore [AgCl] does not appear in the expression for K_{sp}.

Some common solubility products are listed in Table 17.6a according to their K_{sp} values. Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small K_{sp} represents a system in which the equilibrium lies to the left, so that relatively few hydrated ions would be present in a saturated solution.

Table 17.6a Common Solubility Products by Decreasing Equilibrium Constants

Substance	K_{sp} at 25 °C
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
AgI	1.5×10^{-16}
PbS	7×10^{-29}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}

Example 17.6a

Writing Equations and Solubility Products

Write the ionic equation for the dissolution and the solubility product expression for each of the following slightly soluble ionic compounds:

a. AgI, silver iodide, a solid with antiseptic properties
b. $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids
c. $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia
d. $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium
e. $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

(Hint: When determining how to break (d) and (e) up into ions, refer to the list of polyatomic ions in the section on chemical nomenclature.)

Solution

a. $\text{AgI}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{I}^{-}(aq) \qquad K_{\text{sp}} = [\text{Ag}^{+}][\text{I}^{-}]$
b. $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + {\text{CO}_3}^{2-}(aq) \qquad K_{\text{sp}} = [\text{Ca}^{2+}][{\text{CO}_3}^{2-}]$
c. $\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^{-}(aq) \qquad K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$
d. $\text{Mg(NH}_4\text{)PO}_4(s) \rightleftharpoons \text{Mg}^{2+}(aq) + {\text{NH}_4}^{+}(aq) + {\text{PO}_4}^{3-}(aq) \qquad K_{\text{sp}} = [\text{Mg}^{2+}][{\text{NH}_4}^{+}][{\text{PO}_4}^{3-}]$
e. $\text{Ca}_5(\text{PO}_4)3\text{OH}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3{\text{PO}_4}^{3-}(aq) + \text{OH}^{-}(aq) \qquad K_{\text{sp}} = [\text{Ca}^{2+}]^5[{\text{PO}_4}^{3-}]^3[\text{OH}^{-}]$

Exercise 17.6a

Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:

a. $BaSO_4$
b. Ag_2SO_4
c. $Al(OH)_3$
d. $Pb(OH)Cl$

Check Your Answer[1]

Now we will extend the discussion of K_{sp} and show how the solubility product constant is determined from the solubility of its ions, as well as how K_{sp} can be used to determine the molar solubility of a substance.

K_{sp} and Solubility

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M}^{\mathrm{m}+}(aq)\ +\ q\mathrm{X}^{\mathrm{n}\text{-}}(aq)$$

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per litre (mol/L), known as its **molar solubility**.

Example 17.6b

Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF}_2(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq)\ +\ 2\mathrm{F}^-(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15 × 10^{-4} *M*; therefore, that of F^- is 4.30 × 10^{-4} *M*, that is, twice the concentration of Ca^{2+}. What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp}:

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) \ + \ \mathrm{2F^-}(aq)$$

A saturated solution is a solution at equilibrium with the solid. Thus:

$$K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 = (2.1 \ \times \ 10^{-4})(4.2 \ \times \ 10^{-4})^2 = 3.7 \ \times \ 10^{-11}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Exercise 17.6b

Check Your Learning Exercise (Text Version)
In a saturated solution that is in contact with solid $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31 × 10^{-4} *M*. What is the solubility product for $Mg(OH)_2$?

$MgOH_{2(s)} \leftrightarrow Mg^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$

a. 1.31
b. 4.99 x 10^{-6}
c. 1.31 x 10^{-4}
d. 8.99 x 10^{-12}

Check Your Answer[2]

Source: "Exercise 17.6b" is adapted from "Example 15.1-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 17.6c

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3×10^{-9}.

The reaction is:

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu}^{+}(aq) \ + \ \mathrm{Br}^{-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{\mathrm{sp}} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the CuBr column empty as it is a solid and does not contribute to the K_{sp}:

	CuBr $\rightleftharpoons$	Cu^+ +	Br^-
Initial concentration (*M*)		0	0
Change (*M*)		x	x
Equilibrium concentration (*M*)		$0 + x = x$	$0 + x = x$

At equilibrium:

$$K_{\mathrm{sp}} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$
$$6.3 \ \times \ 10^{-9} = (x)(x) = x^2$$
$$x = \sqrt{(6.3 \ \times \ 10^{-9})} = 7.9 \ \times \ 10^{-5}$$

Therefore, the molar solubility of CuBr is 7.9×10^{-5} *M*.

Exercise 17.6c

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Check Your Answer[3]

Example 17.6d

Determination of Molar Solubility from K_{sp}, Part II

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3 × 10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The solubility product constant of calcium hydroxide is 1.3 × 10^{-6}.

The reaction is:

$$\text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) \; + \; 2\text{OH}^-(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

Create an ICE table, leaving the $Ca(OH)_2$ column empty as it is a solid and does not contribute to the K_{sp}:

	$Ca(OH)_2 \rightleftharpoons$	Ca^{2+} +	$2OH^-$
Initial concentration (*M*)		0	0
Change (*M*)		x	$2x$
Equilibrium concentration (*M*)		$0 + x = x$	$0 + 2x = 2x$

At equilibrium:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$
$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$
$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3}$$

Therefore, the molar solubility of $Ca(OH)_2$ is 1.3 × 10^{-2} *M*.

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 1.1×10^{-10}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 17.6b).

Figure 17.6b The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by glitzy queen00, PD)

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Visit Barium X-Rays (Upper and Lower GI) at Johns Hopkins Medicine for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3}^{2-}(aq)$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ($Q = [\mathrm{Ca^{2+}}][\mathrm{CO_3}^{2-}]$) is equal to the solubility product ($K_{sp} = 8.7 \times 10^{-9}$). If we mix a solution of calcium nitrate, which contains $\mathrm{Ca^{2+}}$ ions, with a solution of sodium carbonate, which contains $\mathrm{CO_3}^{2-}$ ions, the slightly soluble ionic solid $\mathrm{CaCO_3}$ will precipitate, provided that the concentrations of $\mathrm{Ca^{2+}}$ and $\mathrm{CO_3}^{2-}$ ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as Example 5 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

Example 17.6e

Precipitation of $\mathrm{Mg(OH)_2}$

The first step in the preparation of magnesium metal is the precipitation of $\mathrm{Mg(OH)_2}$ from sea water by the addition of lime, $\mathrm{Ca(OH)_2}$, a readily available inexpensive source of $\mathrm{OH^-}$ ion:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\mathrm{OH^-}(aq) \qquad K_{sp} = 8.9 \times 10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

This problem asks whether the reaction:

$$\mathrm{Mg(OH)_2}(s) \leftrightharpoons \mathrm{Mg^{2+}}(aq) + 2\mathrm{OH^-}(aq)$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}]$ = 0.0537 *M* and $[OH^-]$ = 0.0010 *M*. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

Example 17.6f

Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}–*M* solution of $AgNO_3$ and a 2.0×10^{-4}–*M* solution of NaCl are mixed?

(Note: The solution also contains Na^+ and NO_3^- ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

The solubility product is 1.6×10^{-10} (see Appendix K).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. The volume doubles when we mix equal volumes of $AgNO_3$ and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[Ag^+]$ and $[Cl^-]$ are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4})\ M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, *Q*, is *momentarily* greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [\mathrm{Ag}^+][\mathrm{Cl}^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} \geq K_{\mathrm{sp}}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with *Q* equal to K_{sp}.

Exercise 17.6d

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of ClO_4^-? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Check Your Answer[4]

In the previous two examples, we have seen that $Mg(OH)_2$ or AgCl precipitate when Q is greater than K_{sp}. In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Example 17.6g

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 17.6c). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4{\cdot}H_2O$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is 2.2 × 10^{-3} *M*. What concentration of $C_2O_4{}^{2-}$ ion must be established before $CaC_2O_4{\cdot}H_2O$ begins to precipitate?

Figure 17.6c Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind, CC BY 2.0)

Solution

The equilibrium expression is:

$$\mathrm{CaC_2O_4}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{C_2O_4}{}^{2-}(aq)$$

For this reaction:

$$K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{C_2O_4}{}^{2-}] = 1.96 \times 10^{-8}$$

(see Appendix K)

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until *Q* equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of $C_2O_4{}^{2-}$ that is necessary to produce the first trace of solid:

$$Q = K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{C_2O_4}{}^{2-}] = 1.96 \times 10^{-8}$$

$$(2.2 \times 10^{-3})[\mathrm{C_2O_4}^{2-}] = 1.96 \times 10^{-8}$$

$$[\mathrm{C_2O_4}^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}$$

A concentration of $C_2O_4^{2-}$ = 8.9 × 10^{-6} M is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 17.6e

If a solution contains 0.0020 mol of CrO_4^{2-} per litre, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Check Your Answer[5]

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in Example 17.6g—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

Example 17.6h

Concentrations Following Precipitation

Clothing washed in water that has a manganese [$Mn^{2+}(aq)$] concentration exceeding 0.1 mg/L (1.8 × 10^{-6} M) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep [Mn^{2+}] equal to 1.8 × 10^{-6} M?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\text{Mn(OH)}_2(s) \rightleftharpoons \text{Mn}^{2+}(aq) + 2\text{OH}^-(aq) \qquad K_{\text{sp}} = 2 \times 10^{-3}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is 1.8×10^{-6} *M*. From that, we calculate the pH. At equilibrium:

$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^-]^2$$

or

$$(1.8 \times 10^{-6})[\text{OH}^-]^2 = 2 \times 10^{-3}$$

so

$$[\text{OH}^-] = 3.3 \times 10^{-4}\ M$$

Now we calculate the pH from the pOH:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(3.3 \times 10 - 4) = 3.48$$
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.80 = 10.52$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.52, the manganese ion will be reduced to a concentration of 1.8×10^{-6} *M*; at that concentration or less, the ion will not stain clothing.

Exercise 17.6f

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which $[Mg^{2+}]$ is diminished to 1.0×10^{-5} *M* by the addition of $Ca(OH)_2$.

Check Your Answer[6]

Due to their light sensitivity, mixtures of silver halides are used in fibre optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{\text{sp}} = 1.6 \times 10^{-10}$), AgBr ($K_{\text{sp}} = 5.0 \times 10^{-13}$), and AgI ($K_{\text{sp}} = 1.5 \times 10^{-16}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp}. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of **selective precipitation**, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 17.6d). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{2-}) are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure 17.6d Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: work by eutrophication&hypoxia, CC BY 2.0)

One common way to remove phosphates from water is by the addition of calcium hydroxide, known as lime, $Ca(OH)_2$. The lime is converted into calcium carbonate, a strong base, in the water. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3(OH)$, which then precipitates out of the solution:

$$5Ca^{2+} + 3PO_4{}^{3-} + OH^- \leftrightharpoons Ca_{10}(PO_4)_6 \cdot (OH)_2(s)$$

The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View Phosphorus Removal – Wastewater for more information on how phosphorus is removed from wastewater.

Common Ion Effect

As we saw when we discussed buffer solutions, the hydronium ion concentration of an aqueous solution of acetic acid decreases when the strong electrolyte sodium acetate, $NaCH_3CO_2$, is added. We can explain this effect using Le Châtelier's principle. The addition of acetate ions causes the equilibrium to shift to the left, decreasing the concentration of H_3O^+ to compensate for the increased acetate ion concentration. This increases the concentration of CH_3CO_2H:

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2{}^-$$

Because sodium acetate and acetic acid have the acetate ion in common, the influence on the equilibrium is called the **common ion effect**.

The common ion effect can also have a direct effect on solubility equilibria. Suppose we are looking at the reaction where silver iodide is dissolved:

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

If we were to add potassium iodide (KI) to this solution, we would be adding a substance that shares a common ion with silver iodide. Le Châtelier's principle tells us that when a change is made to a system at equilibrium, the reaction will shift to counteract that change. In this example, there would be an excess of iodide ions, so the reaction would shift toward the left, causing more silver iodide to precipitate out of solution.

Example 17.6i

Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide ($CdBr_2$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

The first thing you should notice is that the cadmium sulfide is dissolved in a solution that contains cadmium ions. We need to use an ICE table to set up this problem and include the $CdBr_2$ concentration as a contributor of cadmium ions:

$$\text{CdS}(s) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{S}^{2-}(aq)$$

	CdS ⇌	**Cd^{2+} +**	**S^{2-}**
Initial concentration (*M*)		0.010	0
Change (*M*)		x	x
Equilibrium concentration (*M*)		$0.010 + x$	$0 + x = x$

$$K_{\text{sp}} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$
$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$
$$x^2 + 0.010x - 1.0 \times 10^{-28} = 0$$

We can solve this equation using the quadratic formula, but we can also make an assumption to make this calculation much simpler. Since the K_{sp} value is so small compared with the cadmium concentration, we can assume that the change between the initial concentration and the equilibrium concentration is negligible, so that $0.010 + x \sim 0.010$. Going back to our K_{sp} expression, we would now get:

$$K_{\text{sp}} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$
$$(0.010)(x) = 1.0 \times 10^{-28}$$
$$x = 1.0 \times 10^{-26}$$

Therefore, the molar solubility of CdS in this solution is 1.0×10^{-26} *M*.

Exercise 17.6g

Calculate the molar solubility of aluminum hydroxide, $Al(OH)_3$, in a 0.015-*M* solution of aluminum nitrate, $Al(NO_3)_3$. The K_{sp} of $Al(OH)_3$ is 2×10^{-32}.

Check Your Answer[7]

Key Equations

- $M_pX_q(s) \leftrightharpoons pM^{m+}(aq) + qX^{n-}(aq) \qquad K_{sp} = [M^{m+}]^p[X^{n-}]^q$

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "15.1 Precipitation and Dissolution" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*

Notes

1.
   a. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq) \qquad K_{sp} = [Ba^{2+}][SO_4{}^{2-}]$;
   b. $Ag_2SO_4(s) \rightleftharpoons 2Ag^{+}(aq) + SO_4{}^{2-}(aq) \qquad K_{sp} = [Ag^{+}]^2[SO_4{}^{2-}]$;
   c. $Al(OH)_3(s) \rightleftharpoons Al^{2+}(aq) + 3OH^{-}(aq) \qquad K_{sp} = [Al^{3+}][OH^{-}]^3$;
   d. $Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^{-}(aq) + Cl^{-}(aq) \qquad K_{sp} = [Pb^{2+}][OH^{-}][Cl^{-}]$
2. d) 8.99×10^{-12}
3. 1.2×10^{-8} *M*
4. No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$
5. 4.5×10^{-9} *M*
6. 10.97
7. 1×10^{-10} *M*

17.7 RELATIVE STRENGTHS OF ACIDS AND BASES

Learning Objectives

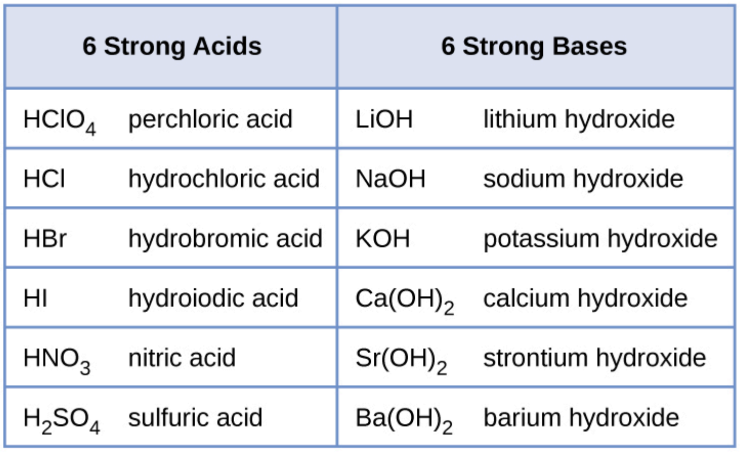
By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) \ + \ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) \ + \ \mathrm{A^-}(aq)$$

Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A^- when the acid ionizes in water; Figure 17.7a lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^-.



6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Figure 17.7a Some of the common strong acids and bases are listed here (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant, K_a**. For the reaction of an acid HA:

$$\mathrm{HA}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{A^-}(aq),$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\ \text{ionization} = \frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 17.7a

Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HNO_2}]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NO_2}^-(aq) + \mathrm{H_3O^+}(aq)$.

Since $10^{-\mathrm{pH}} = [\mathrm{H_3O^+}]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}$ *M*, so that percent ionization is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 17.7a

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89..

Check Your Answer[1]

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq)$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 17.7a lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

Exercise 17.7b

Practice using the following PhET simulation: Acid and Base Solutions

As we did with acids, we can measure the relative strengths of bases by measuring their **base-ionization constant (K_b)** in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\mathrm{B}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq)\ +\ \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

$$K_\mathrm{b} = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$$

where the concentrations are those at equilibrium. Again, we do not include $[H_2O]$ in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

$$\begin{aligned}
\mathrm{NO_2}^-(aq)\ +\ \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{HNO_2}(aq)\ +\ \mathrm{OH^-}(aq) & K_\mathrm{b} &= 2.22\ \times\ 10^{-11}\\
\mathrm{CH_3CO_2}^-(aq)\ +\ \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{CH_3CO_2H}(aq)\ +\ \mathrm{OH^-}(aq) & K_\mathrm{b} &= 5.6\ \times\ 10^{-10}\\
\mathrm{NH_3}(aq)\ +\ \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{NH_4}^+(aq)\ +\ \mathrm{OH^-}(aq) & K_\mathrm{b} &= 1.8\ \times\ 10^{-5}
\end{aligned}$$

As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $HA - A^-$:

$$\mathrm{HA}(aq)\ +\ \mathrm{H_2O}(l)\ \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{A^-}(aq)\quad K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{A^-}(aq)\ +\ \mathrm{H_2O}(l)\ \rightleftharpoons \mathrm{OH^-}(aq)\ +\ \mathrm{HA}(aq)\quad K_\mathrm{b} = \frac{[\mathrm{HA}][\mathrm{OH}]}{[\mathrm{A^-}]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)}\ +\ \mathrm{H_2O}(l)\ +\ \cancel{\mathrm{A^-}(aq)}\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \cancel{\mathrm{A^-}(aq)}\ +\ \mathrm{OH^-}(aq)\ +\ \cancel{\mathrm{HA}(aq)}$$

$$2\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{OH^-}(aq)$$

As shown in the previous chapter on equilibrium, the *K* expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' *K* expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_\mathrm{a}\ \times\ K_\mathrm{b} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}\ \times\ \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_\mathrm{w}$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 17.7b).

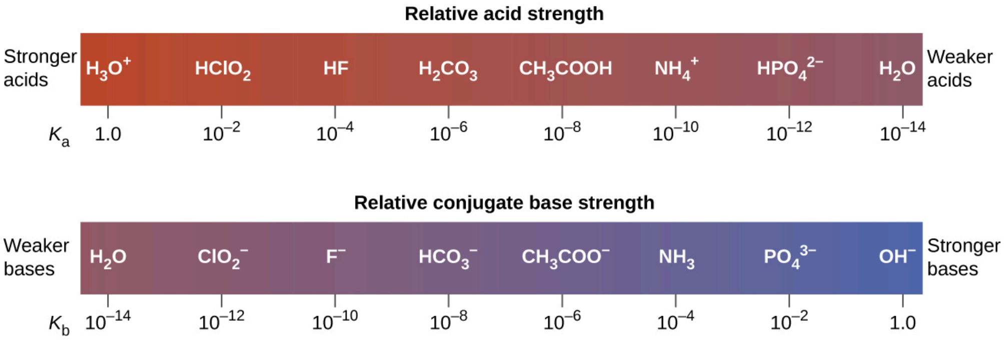
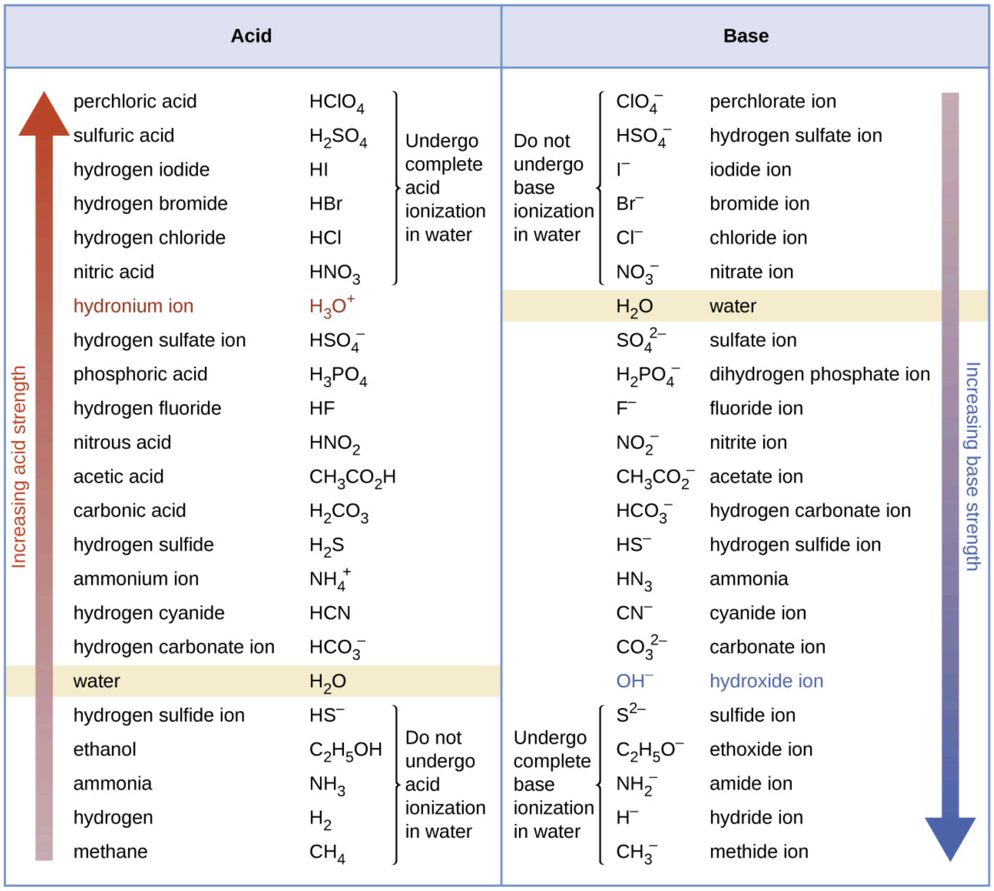


Figure 17.7b This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Figure 17.7c lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.



Acid			Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			HN_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Figure 17.7c The chart shows the relative strengths of conjugate acid-base pairs (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The first six acids in Figure 17.7c are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 17.7c form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 17.7c exhibit no observable acidic behaviour when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 17.7c. A strong base, such as one of those lying below the hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behaviour in aqueous solution.

Example 17.7b

The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17 × 10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Appendix I.

Exercise 17.7c

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Appendix I as 4.9 × 10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8 × 10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Check Your Answer[2]

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid, CH_3CO_2H, is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) \ + \ H_2O(l) \leftrightharpoons H_3O^+(aq) \ + \ CH_3CO_2{}^-(aq),$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 17.7d). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H_3O^+][CH_3CO_2{}^-]}{[CH_3CO_2H]} = 1.8 \ \times \ 10^{-5}$$

Figure 17.7d pH paper indicates that a 0.1-*M* solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 *M*. A 0.1-*M* solution of CH_3CO_2H (beaker on right) is a pH of 3 ($[H_3O^+]$ = 0.001 *M*) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa in *Chemistry (OpenStax)*, CC BY 4.0).

Table 17.7a Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4{}^- + H_2O \rightleftharpoons H_3O^+ + SO_4{}^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2{}^-$	4.6×10^{-4}
$HCNO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2{}^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2{}^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 17.7a gives the ionization constants for several weak acids; additional ionization constants can be found in Appendix I.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq),$$

giving an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 17.7e). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the ionization constant of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$

Figure 17.7e pH paper indicates that a 0.1-*M* solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 *M*) because the weak base NH_3 only partially reacts with water. A 0.1-*M* solution of NaOH (right) has a pOH of 1 because NaOH is a strong base. (credit: modification of work by Sahar Atwa, *Chemistry (OpenStax)*, CC BY 4.0).

The ionization constants of several weak bases are given in Table 17.7b and in Appendix J.

Table 17.7b Ionization Constants of Some Weak Bases

Ionization Reaction	**K_b at 25 °C**
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2{}^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3{}^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3{}^+ + OH^-$	4.3×10^{-10}

Example 17.7c

Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 17.7f); that's why it tastes sour. At equilibrium, a solution contains [CH_3CO_2H] = 0.0787 *M* and [H_3O^+] = [$CH_3CO_2^-$] = 0.00118M. What is the value of K_a for acetic acid?

Figure 17.7f Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by HomeSpot HQ, CC BY 2.0)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CO_2{}^-]}{[CH_3CO_2H]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Exercise 17.7d

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4{}^-(aq) \ + \ H_2O(l) \rightleftharpoons H_3O^+(aq) \ + \ SO_4{}^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*, $[HSO_4^-]$ = 0.29 *M* and $[SO_4^{2-}]$ = 0.13 *M*.

Check Your Answer[3]

Example 17.7d

Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*, $[C_8H_{10}N_4O_2H^+]$ = 5.0 × 10^{-3} *M*, and $[OH^-]$ = 2.5 × 10^{-3} *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2(aq) \ + \ H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) \ + \ OH^-(aq)$$

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \ \times \ 10^{-3})(2.5 \ \times \ 10^{-3})}{0.050} = 2.5 \ \times \ 10^{-4}$$

Exercise 17.7e

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$\mathrm{HPO_4{}^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2PO_4{}^{-}}(aq) + \mathrm{OH^-}(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium, $[OH^-] = 1.3 \times 10^{-6}$ *M*, $[H_2PO_4^-] = 0.042$ *M* and $[HPO_4^{2-}] = 0.341$ *M*.

Check Your Answer[4]

Example 17.7e

Determination of K_a or K_b from pH

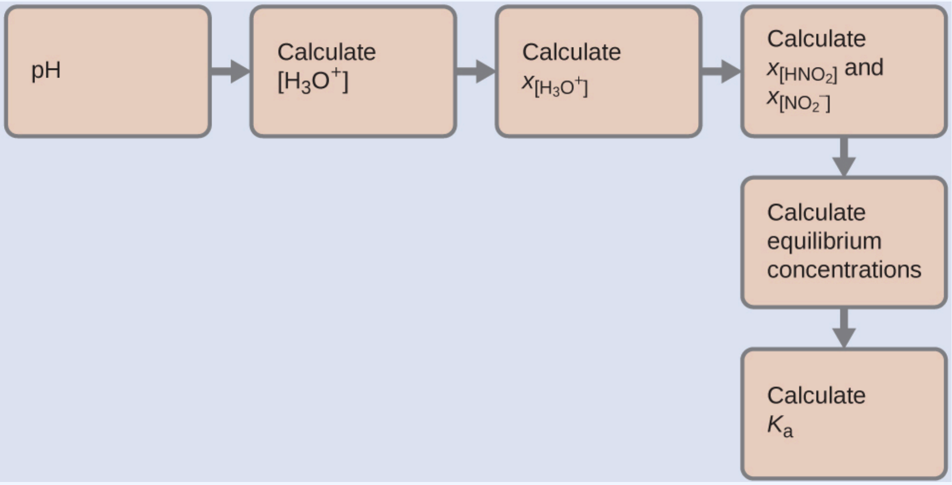
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2{}^{-}}(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):

	HNO_2 +	H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	−*x*	+	*x*	*x*
Equilibrium concentration (*M*)	$[HNO_2]_i$ + (−*x*) = 0.0516 + (−*x*)		$[H_3O]^+$ + *x*$[NO_2]^-$ + *x* ~0 + *x*	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate [H_3O^+, the equilibrium concentration of H_3O^+, from the pH:

$$[\mathrm{H_3O^+}] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[\mathrm{H_3O^+}]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, [H_3O^+]. The initial concentration of $H_3O^+$is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of H_3O^+. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 +	H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	−*x*	+	*x* = 0.0046	*x* = 0.0046
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{NO_2}^-]}{[\mathrm{HNO_2}]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 17.7f

Check Your Learning Exercise (Text Version)
The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3?

a. 1.8×10^{-5}
b. 1.5×10^{-8}
c. 2.4×10^{-5}
d. 1.8×10^{-10}

Check Your Answer[5]

Source: "Exercise 17.7f" is adapted from "Example 14.3-5" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 17.7f

Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings (Figure 17.7g).

Figure 17.7g The pain of an ant's sting is caused by formic acid. (credit: work by John Tann, CC BY 2.0)

What is the concentration of hydronium ion and the pH in a 0.534 *M* solution of formic acid?

$$\mathrm{HCO_2H}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{HCO_2}^-(aq)$$
$$K_\mathrm{a} = 1.8\ \times\ 10^{-4}$$

Solution

1. *Determine x and equilibrium concentrations.* The equilibrium expression is:

$$\mathrm{HCO_2H}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{HCO_2}^-(aq)$$

The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.534 + (-x)$	$0 + x = x$	$0 + x = x$

2. *Solve for x and the equilibrium concentrations.* At equilibrium:

$$\begin{aligned} K_\text{a} &= 1.8 \times 10^{-4} \\ &= \frac{[\text{H}_3\text{O}^+][\text{HCO}_2{}^-]}{[\text{HCO}_2\text{H}]} \\ &= \frac{(x)(x)}{0.534 - x} \end{aligned}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 – x) = 0.534$. This gives:

$$K_\text{a} = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$\begin{aligned} x^2 &= 0.534 \times (1.8 \times 10^{-4}) \\ &= 9.6 \times 10^{-5} \\ x &= \sqrt{9.6 \times 10^{-5}} \\ &= 9.8 \times 10^{-3} \end{aligned}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} \times (100) = \frac{9.8 \times 10^{-3}}{0.534} \times (100) = 1.8\% \leq 5\%$$

since x is less than 5% of the initial concentration (0.534 M), the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$\begin{gathered} [\text{H}_3\text{O}^+] = {\sim}0 + x = 0 + 9.8 \times 10^{-3}\ M. \\ = 9.8 \times 10^{-3}\ M \end{gathered}$$

The pH of the solution can be found by taking the negative log of the $[\text{H}_3\text{O}^+]$, so:

$$-\log(9.8 \times 10^{-3}) = 2.01$$

Exercise 17.7g

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\mathrm{CH_3CO_2H}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{CH_3CO_2{}^-}(aq)$$

$$K_\mathrm{a} = 1.8\ \times\ 10^{-5}$$

(Hint: Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or

$$\frac{[\mathrm{CH_3CO_2{}^-}]}{[\mathrm{CH_3CO_2H}]_\mathrm{initial}}\ \times\ 100$$

Check Your Answer[6]

The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example 17.7g

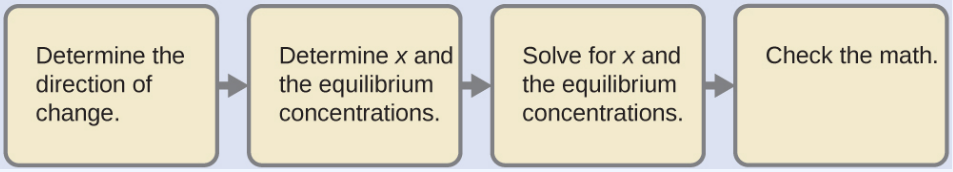
Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25 *M* solution of trimethylamine, a weak base:

$$\mathrm{(CH_3)_3N}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{(CH_3)_3NH^+}(aq)\ +\ \mathrm{OH^-}(aq)$$
$$K_\mathrm{b} = 6.3\ \times\ 10^{-5}$$

Solution

This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 17.7f. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. *Determine x and equilibrium concentrations*. The table shows the changes and concentrations

	$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

2. *Solve for x and the equilibrium concentrations*. At equilibrium:

$$K_\text{b} = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

If we assume that x is small relative to 0.25, then we can replace (0.25 – x) in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$\begin{aligned} [\text{OH}^-] &= \sim 0 + x \\ &= x \\ &= 4.0 \times 10^{-3}\ M \end{aligned}$$

Then calculate pOH as follows:

$$\text{pOH} = -\log(4.0 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_\text{w} = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

3. *Check the work*. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

Example 17.7h

Equilibrium Concentrations in a Solution of a Weak Acid

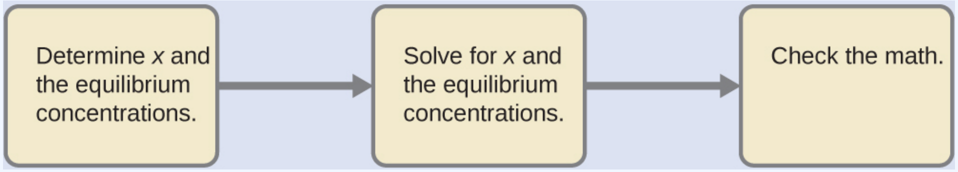
Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4{}^{2-}(aq)$$

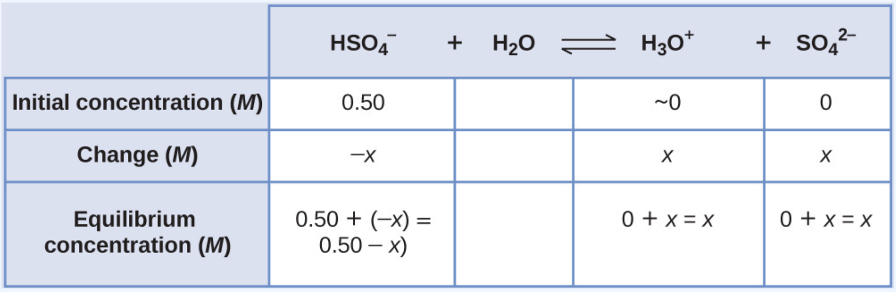
$$K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. *Determine x and equilibrium concentrations.* This table shows the changes and concentrations:



	HSO_4^- +	H_2O ⇌	H_3O^+ +	SO_4^{2-}
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x)$		$0 + x = x$	$0 + x = x$

2. *Solve for x and the concentrations.* As we begin solving for *x*, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of *x*.

   At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4{}^{2-}]}{[HSO_4{}^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that x is small and approximate (0.50 – x) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we calculate:

$$\frac{x}{[HSO_4{}^-]_i} \times (100) = \frac{7.7 \times 10^{-2}}{0.50} \times (100) = 15\%$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^2$$

or

$$x^2 + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^2 + bx + c = 0,$$

x is given by the equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$[H_3O^+] = \sim 0 + x = 0 + 7.2 \times 10^{-2}\ M$$

$$= 7.2 \times 10^{-2}\ M$$

The pH of this solution is:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 7.2 \times 10^{-2} = 1.14$$

Exercise 17.7h

Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+(aq) + \text{OH}^-(aq)$$
$$K_\text{b} = 2.5 \times 10^{-4}$$

(Hint: It will be necessary to convert $[\text{OH}^-]$ to $[\text{H}_3\text{O}^+]$ or pOH to pH toward the end of the calculation.)

Check Your Answer[7]

Key Equations

- $K_\text{a} = \dfrac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
- $K_\text{b} = \dfrac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$
- $K_\text{a} \times K_\text{b} = 1.0 \times 10^{-14} = K_\text{w}$
- $\text{Percent ionization} = \dfrac{[\text{H}_3\text{O}^+]_\text{eq}}{[\text{HA}]_0} \times 100$

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "14.3 Strengths of Acids and Bases" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers,

Notes

1. 1.3% ionized
2. NH_4^+ is the slightly stronger acid (K_a for NH_4^+ = 5.6×10^{-10})
3. K_a for HSO_4^- = $1.2 \text{ x } 10^{-2}$
4. K_b for HPO_4^{2-} = $1.6 \text{ x } 10^{-7}$
5. a) $1.8 \text{ x } 10^{-5}$
6. percent ionization = 1.3%
7. pH 11.16

17.8 REAL WORLD EXAMPLES OF EQUILIBRIA

Learning Objectives

By the end of this section, you will be able to:

- Describe examples of systems involving two (or more) simultaneous chemical equilibria
- Calculate reactant and product concentrations for multiple equilibrium systems
- Compare dissolution and weak electrolyte formation

There are times when one equilibrium reaction does not adequately describe the system being studied. Sometimes we have more than one type of equilibrium occurring at once (for example, an acid-base reaction and a precipitation reaction).

The ocean is a unique example of a system with **multiple equilibria**, or multiple states of solubility equilibria working simultaneously. Carbon dioxide in the air dissolves in sea water, forming carbonic acid (H_2CO_3). The carbonic acid then ionizes to form hydrogen ions and bicarbonate ions (HCO_3^-), which can further ionize into more hydrogen ions and carbonate ions (CO_3^{2-}):

$$\begin{aligned} CO_2(g) &\rightleftharpoons CO_2(aq) \\ CO_2(aq) + H_2O(l) &\rightleftharpoons H_2CO_3(aq) \\ H_2CO_3(aq) &\rightleftharpoons H^+(aq) + HCO_3{}^-(aq) \\ HCO_3{}^-(aq) &\rightleftharpoons H^+(aq) + CO_3{}^{2-}(aq) \end{aligned}$$

The excess H^+ ions make seawater more acidic. Increased ocean acidification can then have negative impacts on reef-building coral, as they cannot absorb the calcium carbonate they need to grow and maintain their skeletons (Figure 17.7a). This in turn disrupts the local biosystem that depends upon the health of the reefs for its survival. If enough local reefs are similarly affected, the disruptions to sea life can be felt globally. The world's oceans are presently in the midst of a period of intense acidification, believed to have begun in the mid-nineteenth century, and which is now accelerating at a rate faster than any change to oceanic pH in the last 20 million years.

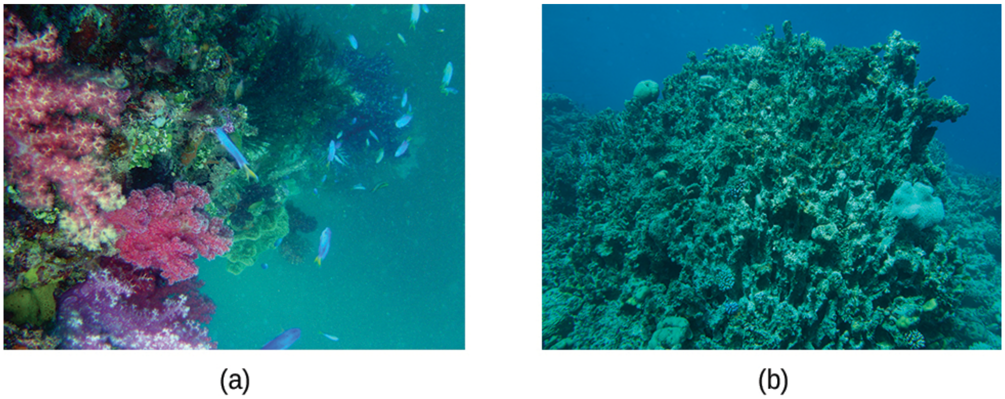


Figure 17.8a Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonite skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library, CC BY 2.0; credit b: modification of work by prilfish, CC BY 2.0)

Watch Can Corals Cope with Ocean Acidification? (3:36 min)

Slightly soluble solids derived from weak acids generally dissolve in strong acids, unless their solubility products are extremely small. For example, we can dissolve $CuCO_3$, FeS, and $Ca_3(PO_4)_2$ in HCl because their basic anions react to form weak acids (H_2CO_3, H_2S, and $H_2PO_4^-$). The resulting decrease in the concentration of the anion results in a shift of the equilibrium concentrations to the right in accordance with Le Châtelier's principle.

Of particular relevance to us is the dissolution of hydroxylapatite, $Ca_5(PO_4)_3OH$, in acid. Apatites are a class of calcium phosphate minerals (Figure 17.7b); a biological form of hydroxylapatite is found as the principal mineral in the enamel of our teeth. A mixture of hydroxylapatite and water (or saliva) contains an equilibrium mixture of solid $Ca_5(PO_4)_3OH$ and dissolved Ca^{2+}, PO_4^{3-}, and OH^- ions:

$$Ca_5(PO_4)_3OH(s) \longrightarrow 5Ca^{2+}(aq) + 3PO_4{}^{3-}(aq) + OH^-(aq)$$

Figure 17.8b Crystal of the mineral hydroxylapatite, $Ca_5(PO_4)_3OH$, is shown here. Pure apatite is white, but like many other minerals, this sample is coloured because of the presence of impurities (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When exposed to acid, phosphate ions react with hydronium ions to form hydrogen phosphate ions and ultimately, phosphoric acid:

$$PO_4{}^{3-}(aq) + H_3O^+ \rightleftharpoons H_2PO_4{}^{2-} + H_2O$$

$$PO_4{}^{2-}(aq) + H_3O^+ \rightleftharpoons H_2PO_4{}^{-} + H_2O$$

$$H_2PO_4{}^{-} + H_3O^+ \rightleftharpoons H_3PO_4 + H_2O$$

Hydroxide ion reacts to form water:

$$OH^-(aq) + H_3O^+ \longrightarrow 2H_2O$$

These reactions decrease the phosphate and hydroxide ion concentrations, and additional hydroxylapatite dissolves in an acidic solution in accord with Le Châtelier's principle. Our teeth develop cavities when acid waste produced by bacteria growing on them causes the hydroxylapatite of the enamel to dissolve. Fluoride toothpastes contain sodium fluoride, NaF, or stannous fluoride [more properly named tin(II) fluoride], SnF_2. They function by replacing the OH^- ion in hydroxylapatite with F^- ion, producing fluorapatite, $Ca_5(PO_4)_3F$:

$$NaF + Ca_5(PO_4)_3OH \rightleftharpoons Ca_5(PO_4)_3F + Na^+ + OH^-$$

The resulting $Ca_5(PO_4)_3F$ is slightly less soluble than $Ca_5(PO_4)_3OH$, and F^- is a weaker base than OH^-. Both of these factors make the fluorapatite more resistant to attack by acids than hydroxylapatite. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Role of Fluoride in Preventing Tooth Decay

As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $Ca_5(PO_4)_3F$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (Figure 17.7c).

Figure 17.8c Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk in *Chemistry (OpenStax)*, CC BY 4.0).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

When acid rain attacks limestone or marble, which are calcium carbonates, a reaction occurs that is similar to the acid attack on hydroxylapatite. The hydronium ion from the acid rain combines with the carbonate ion from calcium carbonates and forms the hydrogen carbonate ion, a weak acid:

$$H_3O^+(aq) + CO_3{}^{2-}(aq) \longrightarrow HCO_3{}^-(aq) + H_2O(l)$$

Calcium hydrogen carbonate, $Ca(HCO_3)_2$, is soluble, so limestone and marble objects slowly dissolve in acid rain.

If we add calcium carbonate to a concentrated acid, hydronium ion reacts with the carbonate ion according to the equation:

$$2H_3O^+(aq) \ + \ CO_3{}^{2-}(aq) \longrightarrow H_2CO_3(aq) \ + \ 2H_2O(l)$$

(Acid rain is usually not sufficiently acidic to cause this reaction; however, laboratory acids are.) The solution may become saturated with the weak electrolyte carbonic acid, which is unstable, and carbon dioxide gas can be evolved:

$$H_2CO_3(aq) \longrightarrow CO_2(g) \ + \ H_2O(l)$$

These reactions decrease the carbonate ion concentration, and additional calcium carbonate dissolves. If enough acid is present, the concentration of carbonate ion is reduced to such a low level that the reaction quotient for the dissolution of calcium carbonate remains less than the solubility product of calcium carbonate, even after all of the calcium carbonate has dissolved.

Example 17.8a

Prevention of Precipitation of $Mg(OH)_2$

Calculate the concentration of ammonium ion that is required to prevent the precipitation of $Mg(OH)_2$ in a solution with $[Mg^{2+}] = 0.10\ M$ and $[NH_3] = 0.10\ M$.

Solution

Two equilibria are involved in this system:

Reaction (1): $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) \ + \ 2OH^-(aq); \qquad K_{sp} = 8.9 \times 10^{-12}$

Reaction (2): $NH_3(aq) \ + \ H_2O(l) \rightleftharpoons NH_4{}^+(aq) \ + \ OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$

To prevent the formation of solid $Mg(OH)_2$, we must adjust the concentration of OH^- so that the reaction quotient for Equation (1), $Q = [Mg^{2+}][OH^-]^2$, is less than K_{sp} for $Mg(OH)_2$. (To simplify the calculation, we determine the concentration of OH^- when $Q = K_{sp}$.) $[OH^-]$ can be reduced by the addition of $NH_4{}^+$, which shifts Reaction (2) to the left and reduces $[OH^-]$.

1. *We determine the $[OH^-]$ at which $Q = K_{sp}$ when $[Mg^{2+}] = 0.10\ M$:*

$$Q = [Mg^{2+}][OH^-]^2 = (0.10)[OH^-]^2 = 8.9 \times 10^{-12}$$
$$[OH^-] = 9.4 \times 10^{-6}\ M$$

Solid $Mg(OH)_2$ will not form in this solution when $[OH^-]$ is less than 1.2×10^{-5} *M*.

2. *We calculate the $[NH_4^+]$ needed to decrease $[OH^-]$ to 1.2×10^{-5} M when $[NH_3] = 0.10$.*

$$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]} = \frac{[NH_4^+](9.4 \times 10^{-6})}{0.10} = 1.8 \times 10^{-5}$$

$$[NH_4{}^+] = 0.19\ M$$

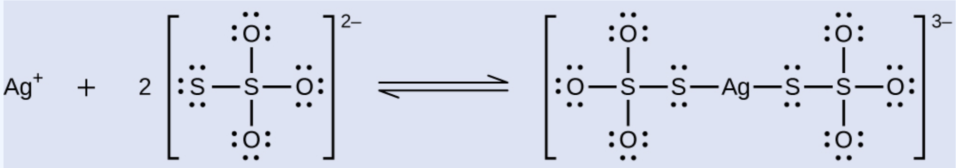
When $[NH_4^+]$ equals 0.19 *M*, $[OH^-]$ will be 9.4×10^{-6} *M*. Any $[NH_4^+]$ greater than 0.19 *M* will reduce $[OH^-]$ below 9.4×10^{-6} *M* and prevent the formation of $Mg(OH)_2$.

Therefore, precise calculations of the solubility of solids from the solubility product are limited to cases in which the only significant reaction occurring when the solid dissolves is the formation of its ions. For formation constants for complex ions, see Appendix L.

Example 17.8b

Multiple Equilibria

Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($Na_2S_2O_3$, called hypo) to form the complex ion $Ag(S_2O_3)_2{}^{3-}$ ($K_f = 4.7 \times 10^{13}$). The reaction with silver bromide is:



What mass of $Na_2S_2O_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $Ag(S_2O_3)_2{}^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $S_2O_3{}^{2-}$ ion:

Reaction (1): $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$

Reaction (2): $Ag^+(aq) + S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq) \qquad K_f = 4.7 \times 10^{13}$

In order for 1.00 g of AgBr to dissolve, the $[Ag^+]$ in the solution that results must be low enough for *Q* for Reaction (1) to be smaller than K_{sp} for this reaction. We reduce [Ag^+] by adding $S_2O_3^{2-}$ and thus cause Reaction (2) to shift to the right. We need the following steps to determine what mass of $Na_2S_2O_3$ is needed to provide the necessary $S_2O_3^{2-}$.

1. *We calculate the [Br^-] produced by the complete dissolution of 1.00 g of AgBr (5.33×10^{-3} mol AgBr) in 1.00 L of solution:*
$$[\mathrm{Br}^-] = 5.33\ \times\ 10^{-3}\ M$$
2. *We use [Br^-] and K_{sp} to determine the maximum possible concentration of Ag^+ that can be present without causing reprecipitation of AgBr:*
$$[\mathrm{Ag}^+] = 9.4\ \times\ 10^{-11}\ M$$
3. *We determine the* [$S_2O_3^{2-}$] *required to make [Ag^+] = 9.4×10^{-11} M after the remaining Ag^+ ion has reacted with $S_2O_3^{2-}$ according to the equation:*
$$\mathrm{Ag}^+\ +\ 2\mathrm{S_2O_3}^{2-} \rightleftharpoons \mathrm{Ag(S_2O_3)_2}^{3-} \qquad K_\mathrm{f} = 4.7\ \times\ 10^{13}$$
Because 5.33×10^{-3} mol of AgBr dissolves:
$$(5.33\ \times\ 10^{-3})\ -\ (9.4\ \times\ 10^{-11}) = 5.33\ \times\ 10^{-3}\ \mathrm{mol\backslash Ag(S_2O_3)_2}^{3-}$$
Thus, at equilibrium: [$Ag(S_2O3)_2^{3-}$] = $5.33 \times 10^{-3} M$, [Ag^+] = $9.4 \times 10^{-11} M$, and $Q = K_f = 4.7 \times 10^{13}$:
$$K_\mathrm{f} = \frac{[\mathrm{Ag(S_2O_3)_2}^{3-}]}{[\mathrm{Ag}^+][\mathrm{S_2O_3}^{2-}]^2} = 4.7\ \times\ 10^{13}$$
$$[\mathrm{S_2O_3}^{2-}] = 1.1\ \times\ 10^{-3}\ M$$
When [$S_2O_3^{2-}$] is $1.1 \times 10^{-3} M$, [Ag^+] is $9.4 \times 10^{-11} M$ and all AgBr remains dissolved.
4. *We determine the total number of moles of* $S_2O_3^{2-}$ *that must be added to the solution.* This equals the amount that reacts with Ag^+ to form $Ag(S_2O3)_2^{3-}$ plus the amount of free $S_2O_3^{2-}$ in solution at equilibrium. To form 5.33×10^{-3} mol of $Ag(S_2O3)_2^{3-}$ requires $2 \times (5.33 \times 10^{-3})$ mol of $S_2O_3^{2-}$. In addition, 1.1×10^{-3} mol of unreacted $S_2O_3^{2-}$ is present (Step 3). Thus, the total amount of $S_2O_3^{2-}$ that must be added is:
$$2\ \times\ (5.33\ \times\ 10^{-3}\ \mathrm{mol\backslash S_2O_3}^{2-})\ +\ 1.1\ \times\ 10^{-3}\ \mathrm{mol\backslash S_2O_3}^{2-} = 1.18\ \times\ 10^{-2}\ \mathrm{mol\backslash S_2O_3}^{2-}$$
5. *We determine the mass of $Na_2S_2O_3$ required to give 1.18×10^{-2} mol* $S_2O_3^{2-}$ *using the molar mass of $Na_2S_2O_3$:*
$$1.18\ \times\ 10^{-2}\ \mathrm{mol\backslash S_2O_3}^{2-}\ \times\ \frac{158.1\ \mathrm{g\backslash Na_2S_2O_3}}{1\ \mathrm{mol\backslash Na_2S_2O_3}} = 1.9\ \mathrm{g\backslash Na_2S_2O_3}$$
Thus, 1.00 L of a solution prepared from 1.9 g $Na_2S_2O_3$ dissolves 1.0 g of AgBr.

Exercise 17.8a

AgCl(*s*), silver chloride, is well known to have a very low solubility: $\text{Ag}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$, $K_{sp} = 1.6 \times 10^{-10}$. Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed: $\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2{}^+(aq)$, $K_f = 1.7 \times 10^7$. What mass of NH_3 is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $Ag(NH_3)_2^+$?

Check Your Answer[1]

Dissolution versus Weak Electrolyte Formation

We can determine how to shift the concentration of ions in the equilibrium between a slightly soluble solid and a solution of its ions by applying Le Châtelier's principle. For example, one way to control the concentration of manganese(II) ion, Mn^{2+}, in a solution is to adjust the pH of the solution and, consequently, to manipulate the equilibrium between the slightly soluble solid manganese(II) hydroxide, manganese(II) ion, and hydroxide ion:

$$\text{Mn(OH)}_2(s) \rightleftharpoons \text{Mn}^{2+}(aq) + 2\text{OH}^-(aq) \qquad K_{sp} = [\text{Mn}^{2+}][\text{OH}^-]^2$$

This could be important to a laundry because clothing washed in water that has a manganese concentration exceeding 0.1 mg per litre may be stained by the manganese. We can reduce the concentration of manganese by increasing the concentration of hydroxide ion. We could add, for example, a small amount of NaOH or some other base such as the silicates found in many laundry detergents. As the concentration of OH^- ion increases, the equilibrium responds by shifting to the left and reducing the concentration of Mn^{2+} ion while increasing the amount of solid $Mn(OH)_2$ in the equilibrium mixture, as predicted by Le Châtelier's principle.

Example 17.8c

Solubility Equilibrium of a Slightly Soluble Solid

What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^{-} when each of the following are added to a mixture of solid $Mg(OH)_2$ in water at equilibrium?

a. $MgCl_2$
b. KOH
c. an acid
d. $NaNO_3$
e. $Mg(OH)_2$

Solution

The equilibrium among solid $Mg(OH)_2$ and a solution of Mg^{2+} and OH^{-} is:

$$\mathbf{Mg(OH)_2}(s) \rightleftharpoons \mathbf{Mg^{2+}}(aq) \ + \ \mathbf{2OH^{-}}(aq)$$

a. The reaction shifts to the left to relieve the stress produced by the additional Mg^{2+} ion, in accordance with Le Châtelier's principle. In quantitative terms, the added Mg^{2+} causes the reaction quotient to be larger than the solubility product ($Q > K_{sp}$), and $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^{-}]$ is less and $[Mg^{2+}]$ is greater than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.
b. The reaction shifts to the left to relieve the stress of the additional OH^{-} ion. $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^{-}]$ is greater and $[Mg^{2+}]$ is less than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.
c. The concentration of OH^{-} is reduced as the OH^{-} reacts with the acid. The reaction shifts to the right to relieve the stress of less OH^{-} ion. In quantitative terms, the decrease in the OH^{-} concentration causes the reaction quotient to be smaller than the solubility product ($Q < K_{sp}$), and additional $Mg(OH)_2$ dissolves until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^{-}]$ is less and $[Mg^{2+}]$ is greater than in the solution of $Mg(OH)_2$ in pure water. More $Mg(OH)_2$ is dissolved.
d. $NaNO_3$ contains none of the species involved in the equilibrium, so we should expect that it has no appreciable effect on the concentrations of Mg^{2+} and OH^{-}. (As we have seen previously, dissolved salts change the activities of the ions of an electrolyte. However, the salt effect is generally small, and we shall neglect the slight errors that may result from it.)
e. The addition of solid $Mg(OH)_2$ has no effect on the solubility of $Mg(OH)_2$ or on the concentration

of Mg^{2+} and OH^{-}. The concentration of $Mg(OH)_2$ does not appear in the equation for the reaction quotient:

$$Q=[\mathrm{Mg}^{2+}][\mathrm{OH}^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of *Q*, and no shift is required to restore *Q* to the value of the equilibrium constant.

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Notes

1. 1.00 L of a solution prepared with 4.81 g NH_3 dissolves 2.0 g of AgCl.

CHAPTER 17 - SUMMARY

17.1 Chemical Reaction Rates

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

17.2 Chemical Equilibria

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

17.3 Equilibrium Constants

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

17.4 Shifting Equilibria: Le Châtelier’s Principle

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system’s response to these disturbances is described by Le Châtelier’s principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

17.5 Equilibrium Calculations

The ratios of the rate of change in concentrations of a reaction are equal to the ratios of the coefficients in the balanced chemical equation. The sign of the coefficient of X is positive when the concentration increases and negative when it decreases. We learned to approach three basic types of equilibrium problems. When given the concentrations of the reactants and products at equilibrium, we can solve for the equilibrium constant; when given the equilibrium constant and some of the concentrations involved, we can solve for the missing concentrations; and when given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium.

17.6 Precipitation and Dissolution

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp}, of the solid. When we have a heterogeneous equilibrium involving the slightly soluble solid M_pX_q and its ions M^{m+} and X^{n-}:

$$\mathrm{M}_p\mathrm{X}_q(s) \leftrightharpoons p\mathrm{M}^{\mathrm{m}+}(aq) \ + \ q\mathrm{X}^{\mathrm{n}-}(aq)$$

We write the solubility product expression as:

$$K_{\mathrm{sp}} = [\mathrm{M}^{\mathrm{m}+}]^p[\mathrm{X}^{\mathrm{n}-}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp}, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions.

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product.

A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Châtelier’s principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

17.7 Relative Strengths of Acids and Bases

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

17.8 Real World Examples of Equilibria

Several systems we encounter consist of multiple equilibria, systems where two or more equilibria processes are occurring simultaneously. Some common examples include acid rain, fluoridation, and dissolution of carbon dioxide in sea water. When looking at these systems, we need to consider each equilibrium separately and then combine the individual equilibrium constants into one solubility product or reaction quotient expression using the tools from the first equilibrium chapter. Le Châtelier's principle also must be considered, as each reaction in a multiple equilibria system will shift toward reactants or products based on what is added to the initial reaction and how it affects each subsequent equilibrium reaction.

Attribution & References

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CHAPTER 17 - REVIEW

17.1 Chemical Reaction Rates

1. What is the difference between average rate, initial rate, and instantaneous rate? **Check Answer:** [1]
2. Ozone decomposes to oxygen according to the equation $2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.
3. In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $\text{Cl}_2(g) + 3\text{F}_2(g) \longrightarrow 2\text{ClF}_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3. **Check Answer:** [2]
4. A study of the rate of dimerization of C_4H_6 gave the data shown in the table below:
   $2\text{C}_4\text{H}_6 \longrightarrow \text{C}_8\text{H}_{12}$

Time (s)	0	1600	3200	4800	6200
[C_4H_6] (*M*)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

   a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
   b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus [C_4H_6]. What are the units of this rate?
   c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).
5. A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data as shown in the table below:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[*A*] (*M*)	1.00	0.952	0.625	0.465	0.370	0.308	0.230

   a. Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
   b. Estimate the instantaneous rate of disappearance of *A* at 15.0 s from a graph of time versus [*A*].

What are the units of this rate?
   c. Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.
   Check Answer: [3]

6. Consider the following reaction in aqueous solution:
   $5\text{Br}^-(aq) + \text{BrO}_3{}^-(aq) + 6\text{H}^+(aq) \longrightarrow 3\text{Br}_2(aq) + 3\text{H}_2\text{O}(l)$

   If the rate of disappearance of $\text{Br}^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4} M\,s^{-1}$, what is the rate of appearance of $\text{Br}_2(aq)$ at that moment?

17.2 Chemical Equilibria

1. What does it mean to describe a reaction as "reversible"? **Check Answer:** [4]
2. When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?
3. If a reaction is reversible, when can it be said to have reached equilibrium? **Check Answer:** [5]
4. Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?
5. If the concentrations of products and reactants are equal, is the system at equilibrium? **Check Answer:** [6]

17.3 Equilibrium Constants

1. Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.
2. Explain why an equilibrium between $\text{Br}_2(l)$ and $\text{Br}_2(g)$ would not be established if the container were not a closed vessel. **Check Answer:** [7]
3. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?
   $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$
4. Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, PbCl_2, and CuCl.
   a. Write the expression for the equilibrium constant for the reaction represented by the equation $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
   b. Write the expression for the equilibrium constant for the reaction represented by the equation $\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{PbCl}_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
   Check Answer: [8]
5. Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and

arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
b. Write the expression for the equilibrium constant for the reaction represented by the equation $3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq) \rightleftharpoons Ba_3(PO_4)_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

6. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer. **Check Answer:** [9]
7. Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI(aq) + I_2(aq) \rightleftharpoons KI_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and $I_3{}^-$.
8. For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction? **Check Answer:** [10]
9. For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?
10. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:
    a. $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$
    b. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
    c. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
    d. $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$
    e. $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$
    f. $Br_2(g) \rightleftharpoons 2Br(g)$
    g. $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$
    h. $CuSO_4{\cdot}5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

    Check Answer: [11]
11. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:
    a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
    b. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
    c. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
    d. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
    e. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
    f. $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$
    g. $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$
    h. $S_8(g) \rightleftharpoons 8S(g)$

12. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.
    a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; [NH_3] = 0.20 *M*, [N_2] = 1.00 *M*, [H_2] = 1.00 *M*
    b. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 3.0 atm, N_2 = 2.0 atm, H_2 = 1.0 atm
    c. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; [SO_3] = 0.00 *M*, [SO_2] = 1.00 *M*, [O_2] = 1.00 *M*
    d. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 16.5$; initial pressures: SO_3 = 1.00 atm, SO_2 = 1.00 atm, O_2 = 1.00 atm
    e. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_c = 4.6 \times 10^4$; [NO] = 1.00 *M*, [Cl_2] = 1.00 *M*, [NOCl] = 0 *M*
    f. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_P = 0.050$; initial pressures: NO = 10.0 atm, N_2 = O_2 = 5 atm

    Check Answer: [12]
13. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.
    a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; [NH_3] = 0.50 *M*, [N_2] = 0.15 *M*, [H_2] = 0.12 *M*
    b. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 2.00 atm, N_2 = 10.00 atm, H_2 = 10.00 atm
    c. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; [SO_3] = 2.00 *M*, [SO_2] = 2.00 *M*, [O_2] = 2.00 *M*
    d. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 6.5 \text{ atm}$; initial pressures: SO_2 = 1.00 atm, O_2 = 1.130 atm, SO_3 = 0 atm
    e. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_P = 2.5 \times 10^3$; initial pressures: NO = 1.00 atm, Cl_2 = 1.00 atm, NOCl = 0 atm
    f. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.050$; [N_2] = 0.100 *M*, [O_2] = 0.200 *M*, [NO] = 1.00 *M*
14. The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

    $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

    If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? *P*(NH_3) = 93 atm, *P*(N_2) = 48 atm, and *P*(H_2) = 52 **Check Answer:** [13]
15. Determine if the following system is at equilibrium. If not, in which direction will the system need to

shift to reach equilibrium?

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

$[SO_2Cl_2]$ = 0.12 M, $[Cl_2]$ = 0.16 M and $[SO_2]$ = 0.050 M. K_c for the reaction is 0.078.

16. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.
    a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ ^\circ\text{C}$
    b. $H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ\text{C}$
    c. $Na_2SO_4{\cdot}10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \qquad K_P = 4.08 \times 10^{-25} \text{ at } 25\ ^\circ\text{C}$
    d. $H_2O(l) \rightleftharpoons H_2O(g) \qquad K_P = 0.122 \text{ at } 50\ ^\circ\text{C}$

    Check Answer: [14]
17. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.
    a. $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad K_c = 4.7 \times 10^{-2} \text{ at } 25\ ^\circ\text{C}$
    b. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_P = 48.2 \text{ at } 500\ ^\circ\text{C}$
    c. $CaCl_2{\cdot}6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \qquad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ\text{C}$
    d. $H_2O(l) \rightleftharpoons H_2O(g) \qquad K_P = 0.196 \text{ at } 60\ ^\circ\text{C}$
18. What is the value of the equilibrium constant expression for the change $H_2O(l) \rightleftharpoons H_2O(g)$ at 30 °C? **Check Answer:** [15]
19. Write the expression of the reaction quotient for the ionization of HOCN in water.
20. Write the reaction quotient expression for the ionization of NH_3 in water.**Check Answer:** [16]
21. What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (Vapour pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

17.4 Shifting Equilibria: Le Châtelier's Principle

1. The following equation represents a reversible decomposition:

   $$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

   Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains? **Check Answer:** [17]
2. Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.
3. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant? **Check Answer:** [18]
4. What would happen to the colour of the solution in part (b) of Figure 17.4a if a small amount of NaOH were added and $Fe(OH)_3$ precipitated? Explain your answer.
5. The following reaction occurs when a burner on a gas stove is lit:

$$CH_4(g)\ +\ 2O_2(g) \rightleftharpoons CO_2(g)\ +\ 2H_2O(g)$$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer. **Check Answer:** [19]

6. A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.
   $$2SO_2(g)\ +\ O_2(g) \longrightarrow 2SO_3(g)$$
   a. Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
   b. Is the reaction endothermic or exothermic?
7. Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:
   $$P_4(g)\ +\ 6H_2(g) \rightleftharpoons 4PH_3(g) \qquad \Delta H = 110.5\text{ kJ}$$
   Check Answer: [20]
8. Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction:
   $H_2O(g)\ +\ C(s) \rightleftharpoons H_2(g)\ +\ CO(g)$. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.
   a. Write the expression for the equilibrium constant (K_c) for the reversible reaction
   $$2H_2(g)\ +\ CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.2\text{ kJ}$$
   b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
   c. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?
   d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?
   e. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?
   f. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?
9. Nitrogen and oxygen react at high temperatures.
   a. Write the expression for the equilibrium constant (K_c) for the reversible reaction
   $$N_2(g)\ +\ O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181\text{ kJ}$$
   b. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?
   c. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

   d. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?
   e. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
   f. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?
   g. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?
      Check Answer:
10. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.
    a. Write the expression for the equilibrium constant for the reversible reaction
       $\mathrm{C}(s) \ + \ \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) \ + \ \mathrm{H_2}(g) \qquad \Delta H = 131.30 \text{ kJ}$
    b. What will happen to the concentration of each reactant and product at equilibrium if more C is added?
    c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
    d. What will happen to the concentration of each reactant and product at equilibrium if CO is added?
    e. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?
11. Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.
    a. Write the expression for the equilibrium constant (K_c) for the reversible reaction
       $\mathrm{Fe_2O_3}(s) \ + \ 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{Fe}(s) \ + \ 3\mathrm{H_2O}(g) \qquad \Delta H = 98.7 \text{ kJ}$
    b. What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
    c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
    d. What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?
    e. What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
    f. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?
       Check Answer: [21]
12. Ammonia is a weak base that reacts with water according to this equation:
    $\mathrm{NH_3}(aq) \ + \ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4}^+(aq) \ + \ \mathrm{OH}^-(aq)$
    Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?
    a. Addition of NaOH

   b. Addition of HCl
   c. Addition of NH_4Cl

13. Acetic acid is a weak acid that reacts with water according to this equation:

    $$CH_3CO_2H(aq)\ +\ H_2O(aq) \rightleftharpoons H_3O^+(aq)\ +\ CH_3CO_2{}^-(aq)$$

    Will any of the following increase the percent of acetic acid that reacts and produces $CH_3CO_2^-$ ion?
    a. Addition of HCl
    b. Addition of NaOH
    c. Addition of $NaCH_3CO_2$

    Check Answer: [22]

14. Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

    $$Na^+(aq)\ +\ Cl^-(aq)\ +\ Ag^+(aq)\ +\ NO_3{}^-(aq) \rightleftharpoons AgCl(s)\ +\ Na^+(aq)\ +\ NO_3{}^-(aq)$$

    $$\Delta H = -65.9\ \text{kJ}$$

15. How can the pressure of water vapor be increased in the following equilibrium?

    $$H_2O(l) \rightleftharpoons H_2O(g) \qquad \Delta H = 41\ \text{kJ}$$

    Check Answer: [23]

16. Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.

    $$2Ag^+(aq)\ +\ SO_4{}^{2-}(aq) \rightleftharpoons Ag_2SO_4(s)$$

    Which of the following will occur?
    a. Ag^+ or SO_4^{2-} concentrations will not change.
    b. The added silver sulfate will dissolve.
    c. Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine.
    d. The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

17. The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization $(HX \rightleftharpoons H^+\ +\ X^-)$?

    Check Answer: [24]

17.5 Equilibrium Calculations

1. A reaction is represented by this equation: $A(aq)\ +\ 2B(aq) \rightleftharpoons 2C(aq) \qquad K_c = 1\ \times\ 10^3$
   a. Write the mathematical expression for the equilibrium constant.
   b. Using concentrations ≤1 M, make up two sets of concentrations that describe a mixture of A, B,

and C at equilibrium.

Check Answer: [25]

2. A reaction is represented by this equation:

   $$2\text{W}(aq) \rightleftharpoons \text{X}(aq) + 2\text{Y}(aq) \qquad K_c = 5 \times 10^{-4}$$

   a. Write the mathematical expression for the equilibrium constant.
   b. Using concentrations of ≤1 M, make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.
3. What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

   $$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$

   An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 M H_2, 1.15 M N_2, and $4.12 \times 10^{-1} M$ NH_3.

   Check Answer: [26]
4. Hydrogen is prepared commercially by the reaction of methane and water vapour at elevated temperatures.

   $$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons 3\text{H}_2(g) + \text{CO}(g)$$

   What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 M; H_2O, 0.242 M; CO, 0.126 M; H_2 1.15 M, at a temperature of 760 °C?
5. A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature. **Check Answer:** [27]
6. At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 M is 3.3×10^{-3}% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

   $$2\text{NO}_2(g) \rightleftharpoons 2\text{NO}(g) + \text{O}_2(g)$$
7. Calculate the value of the equilibrium constant K_P for the reaction $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm. **Check Answer:** [28]
8. When heated, iodine vapor dissociates according to this equation:

   $$\text{I}_2(g) \rightleftharpoons 2\text{I}(g)$$

   At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.
9. A sample of ammonium chloride was heated in a closed container.

   $$\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$$

   At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature? **Check Answer:** [29]
10. At a temperature of 60 °C, the vapour pressure of water is 0.196 atm. What is the value of the

equilibrium constant K_P for the transformation at 60 °C?

$$H_2O(l) \rightleftharpoons H_2O(g)$$

11. Complete the changes in concentrations (or pressure, if requested) for each of the following reactions in the table below.

a.		$2\,SO_{3\,(g)}$	$\rightleftharpoons$	$2\,SO_{2\,(g)}$	$+\,O_{2\,(g)}$
		______		______	+x
		______		______	0.125 M
b.	$4\,NH_{3\,(g)}$	$+\,3\,O_{2\,(g)}$	$\rightleftharpoons$	$2\,N_{2\,(g)}$	$+\,6\,H_2O_{\,(g)}$
	______	3x		______	______
	______	0.24 M		______	______
c.		$2\,CH_{4\,(g)}$	$\rightleftharpoons$	$C_2H_{2\,(g)}$	$+\,3\,H_{2\,(g)}$
		______		x	______
		______		25 torr	______
d.	$CH_{4\,(g)}$	$+\,H_2O_{\,(g)}$	$\rightleftharpoons$	$CO_{\,(g)}$	$+\,3\,H_{2\,(g)}$
	______	x		______	______
	______	5 atm		______	______
e.		$NH_4Cl_{\,(s)}$	$\rightleftharpoons$	$NH_{3\,(g)}$	$+\,HCl_{\,(g)}$
				x	______
				1.03 x 10^{-4} M	______
f.	$Ni_{\,(s)}$	$+\,4\,CO_{\,(g)}$	$\rightleftharpoons$	$Ni(CO)_{4\,(g)}$	
		4x		______	
		0.40 atm		______	

Check Answer: [30]

12. Complete the changes in concentrations (or pressure, if requested) for each of the following reactions in the table below.

a.	$2\ H_2\ (g)$	$+\ O_2\ (g)$	$\rightleftharpoons$	$2\ H_2O\ (g)$	
	______	______		+2x	
	______	______		1.50 M	
b.	$CS_2\ (g)$	$+\ 4\ H_2\ (g)$	$\rightleftharpoons$	$CH_4\ (g)$	$+\ 2\ H_2S\ (g)$
	x	______		______	______
	0.020 M	______		______	______
c.	$H_2\ (g)$	$+\ Cl_2\ (g)$	$\rightleftharpoons$	$2\ HCl\ (g)$	
	x	______		______	
	1.50 atm	______		______	
d.	$2\ NH_3\ (g)$	$+\ 2\ O_2\ (g)$	$\rightleftharpoons$	$N_2O\ (g)$	$+\ 3\ H_2O\ (g)$
	______	______		______	x
	______	______		______	60.6 torr
e.		$NH_4HS\ (s)$	$\rightleftharpoons$	$NH_3\ (g)$	$+\ H_2S\ (g)$
				x	______
				9.8×10^{-6} M	______
f.	$Fe\ (s)$	$+\ 5\ CO\ (g)$	$\rightleftharpoons$	$Fe(CO)_4\ (g)$	
		______		x	
		______		0.012 atm	

13. Why are there no changes specified for Ni in Exercise 11, part (f) above? What property of Ni does change? **Check Answer:** [31]
14. Why are there no changes specified for NH_4HS in Exercise 12, part (e) above? What property of NH_4HS does change?
15. Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

    $$N_2(g)\ +\ 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ ^\circ\text{C}$$

    Calculate the equilibrium molar concentration of NH_3. **Check Answer:** [32]
16. Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

    $$H_2\ +\ I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ\text{C}$$

17. What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?
    $$\mathrm{Cl_2}(g) \ + \ \mathrm{Br_2}(g) \rightleftharpoons 2\mathrm{BrCl}(g) \qquad K_P = 4.7 \ \times \ 10^{-2}$$
    Check Answer: [33]
18. What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?
    $$\mathrm{H_2}(g) \ + \ \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2O}(g) \ + \ \mathrm{CO}(g) \qquad K_P = 1.6 \text{ at } 990\ ^\circ\mathrm{C}$$
19. Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.
    $$\mathrm{CoO}(s) \ + \ \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) \ + \ \mathrm{CO_2}(g) \qquad K_c = 4.90 \ \times \ 10^2 \text{ at } 550\ ^\circ\mathrm{C}$$
    What concentration of CO remains in an equilibrium mixture with $[CO_2]$ = 0.100 *M*? **Check Answer:** [34]
20. Carbon reacts with water vapour at elevated temperatures.
    $$\mathrm{C}(s) \ + \ \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) \ + \ \mathrm{H_2}(g) \qquad K_c = 0.2 \text{ at } 1000\ ^\circ\mathrm{C}$$
    What is the concentration of CO in an equilibrium mixture with $[H_2O]$ = 0.500 *M* at 1000 °C?
21. Sodium sulfate 10–hydrate, $Na_2SO_4{\cdot}10H_2O$, dehydrates according to the equation
    $$\mathrm{Na_2SO_4{\cdot}10H_2O}(s) \rightleftharpoons \mathrm{Na_2SO_4}(s) \ + \ 10\mathrm{H_2O}(g) \qquad K_P = 4.08 \ \times \ 10^{-25} \text{ at } 25\ ^\circ\mathrm{C}$$
    What is the pressure of water vapour at equilibrium with a mixture of $Na_2SO_4{\cdot}10H_2O$ and $NaSO_4$? **Check Answer:** [35]
22. Calcium chloride 6–hydrate, $CaCl_2{\cdot}6H_2O$, dehydrates according to the equation
    $$\mathrm{CaCl_2{\cdot}6H_2O}(s) \rightleftharpoons \mathrm{CaCl_2}(s) \ + \ 6\mathrm{H_2O}(g) \qquad K_P = 5.09 \ \times \ 10^{-44} \text{ at } 25\ ^\circ\mathrm{C}$$
    What is the pressure of water vapour at equilibrium with a mixture of $CaCl_2{\cdot}6H_2O$ and $CaCl_2$?
23. A student solved the following problem and found the equilibrium concentrations to be $[SO_2]$ = 0.590 *M*, $[O_2]$ = 0.0450 *M*, and $[SO_3]$ = 0.260 *M*. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:
    $$2\mathrm{SO_2}(g) \ + \ \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{SO_3}(g) \qquad K_c = 4.32$$
    What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3]$ = 0.500 *M*, $[SO_2]$ = 0 *M*, and $[O_2]$ = 0.350 *M*? **Check Answer:** [36]
24. A student solved the following problem and found $[N_2O_4]$ = 0.16 *M* at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?
    $$2\mathrm{NO_2}(g) \rightleftharpoons \mathrm{N_2O_4}(g) \qquad K_c = 160$$
25. Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.
    a. Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.
    $$\mathrm{N_2O_4}(g) \leftrightharpoons 2\mathrm{NO_2}(g) \qquad K_c = 1.07 \ \times \ 10^{-5} \text{ in chloroform}$$

   b. Show that the change is small enough to be neglected.
   Check Answer: [37]

26. Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.
    a. Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.
    $$\mathrm{COCl_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{Cl_2}(g) \qquad K_c = 2.2 \times 10^{-10}$$
    b. Show that the change is small enough to be neglected.
27. Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.
    a. Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.
    $$2\mathrm{H_2S}(g) \rightleftharpoons 2\mathrm{H_2}(g) + \mathrm{S_2}(g) \qquad K_P = 2.2 \times 10^{-6}$$
    b. Show that the change is small enough to be neglected. **Check Answer:** [38]
28. What are all concentrations after a mixture that contains $[H_2O]$ = 1.00 *M* and $[Cl_2O]$ = 1.00 *M* comes to equilibrium at 25 °C?
    $$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\mathrm{HOCl}(g) \qquad K_c = 0.0900$$
29. What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5]$ = 2.00 *M*?
    $$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \qquad K_c = 0.0211$$
    Check Answer: [39]
30. Calculate the pressures of all species at equilibrium in a mixture of NOCl, NO, and Cl_2 produced when a sample of NOCl with a pressure of 10.0 atm comes to equilibrium according to this reaction:
    $$2\mathrm{NOCl}(g) \rightleftharpoons 2\mathrm{NO}(g) + \mathrm{Cl_2}(g) \qquad K_P = 4.0 \times 10^{-4}$$
31. Calculate the equilibrium concentrations of NO, O_2, and NO_2 in a mixture at 250 °C that results from the reaction of 0.20 *M* NO and 0.10 *M* O_2. (Hint: *K* is large; assume the reaction goes to completion then comes back to equilibrium.) **Check Answer:** [40]
    $$2\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO_2}(g) \qquad K_c = 2.3 \times 10^5 \text{ at } 250\ ^\circ\mathrm{C}$$
32. Calculate the equilibrium concentrations that result when 0.25 *M* O_2 and 1.0 *M* HCl react and come to equilibrium.
    $$4\mathrm{HCl}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{Cl_2}(g) + 2\mathrm{H_2O}(g) \qquad K_c = 3.1 \times 10^{13}$$
33. One of the important reactions in the formation of smog is represented by the equation
    $$\mathrm{O_3}(g) + \mathrm{NO}(g) \rightleftharpoons \mathrm{NO_2}(g) + \mathrm{O_2}(g) \qquad K_P = 6.0 \times 10^{34}$$
    What is the pressure of O_3 remaining after a mixture of O_3 with a pressure of 1.2×10^{-8} atm and NO with a pressure of 1.2×10^{-8} atm comes to equilibrium? (Hint: K_P is large; assume the reaction goes to completion then comes back to equilibrium.) **Check Answer:** [41]
34. Calculate the pressures of NO, Cl_2, and NOCl in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm NO and 2.0 atm Cl_2. (Hint: K_P is small; assume the reverse reaction goes

to completion then comes back to equilibrium.)

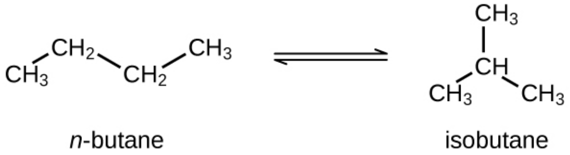
$$2NO(g)\ +\ Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_P = 2.5\ \times\ 10^3$$

35. Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

    $$H_2\ +\ I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ C$$

    Check Answer: [42]

36. Butane exists as two isomers, *n*−butane and isobutane shown in the figure below with K_P = 2.5 at 25 °C.

    What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

37. What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.050 for the decomposition reaction of $CaCO_3$ at that temperature?

    $$CaCO_3(s) \rightleftharpoons CaO(s)\ +\ CO_2(g)$$

    Check Answer: [43]

38. The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

    $$H_2(g)\ +\ CO_2(g) \rightleftharpoons H_2O(g)\ +\ CO(g)$$

    Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

39. At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are $P_{N_2O_4} = 0.70$ atm and $P_{NO_2} = 0.30$ atm.
    a. Predict how the pressures of NO_2 and N_2O_4 will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?
    b. Calculate the partial pressures of NO_2 and N_2O_4 when they are at equilibrium at 9.0 atm and 25 °C. **Check Answer:** [44]

40. In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

    $$N_2(g)\ +\ 3H_2(g) \rightleftharpoons 2NH_3(g)$$

    a. How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
    b. Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

41. The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

   a. On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapour, and 0.90 mol of H_2 in a litre. How many moles of CO_2 were there in the equilibrium mixture?
   b. Maintaining the same temperature, additional H_2 was added to the system, and some water vapour was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapour, and 1.2 mol of H_2 in a litre. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapour concentration to be the same in the two equilibrium solutions even though some vapour was removed before the second equilibrium was established. **Check Answer:** [45]

42. Antimony pentachloride decomposes according to this equation:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

43. Consider the reaction between H_2 and O_2 at 1000 K

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K_P = \frac{(P_{H_2O})^2}{(P_{O_2})(P_{H_2})^3} = 1.33 \times 10^{20}$$

If 0.500 atm of H_2 and 0.500 atm of O_2 are allowed to come to equilibrium at this temperature, what are the partial pressures of the components? **Check Answer:** [46]

44. An equilibrium is established according to the following equation

$$Hg_2{}^{2+}(aq) + NO_3{}^-(aq) + 3H^+(aq) \rightleftharpoons 2Hg^{2+}(aq) + HNO_2(aq) + H_2O(l) \qquad K_c = 4.6$$

What will happen in a solution that is 0.20 *M* each in $Hg_2{}^{2+}$, $NO_3{}^-$, H^+, Hg^{2+}, and HNO_2?

   a. $Hg_2{}^{2+}$ will be oxidized and $NO_3{}^-$ reduced.
   b. $Hg_2{}^{2+}$ will be reduced and $NO_3{}^-$ oxidized.
   c. Hg^{2+} will be oxidized and HNO_2 reduced.
   d. Hg^{2+} will be reduced and HNO_2 oxidized.
   e. There will be no change because all reactants and products have an activity of 1.

45. Consider the equilibrium

$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$

   a. What is the expression for the equilibrium constant (K_c) of the reaction?
   b. How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
   c. If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of NO_2?

   d. If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change? **Check Answer:** [47]

46. The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

    $\mathrm{HbO_2}(aq) \ + \ \mathrm{H_3O^+}(aq) \ + \ \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CO_2} \ - \ \mathrm{Hb} \ - \ \mathrm{H^+} \ + \ \mathrm{O_2}(g) \ + \ \mathrm{H_2O}(l)$

    1. Write the equilibrium constant expression for this reaction.
    2. Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

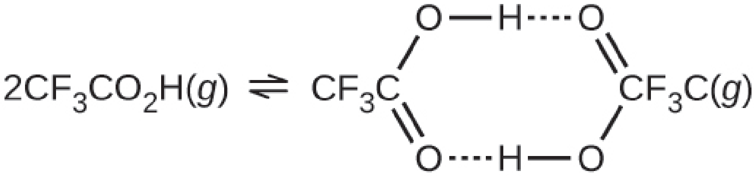
47. The hydrolysis of the sugar sucrose to the sugars glucose and fructose follows a first-order rate equation for the disappearance of sucrose.

    $$\mathrm{C_{12}H_{22}O_{11}}(aq) \ + \ \mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(aq) \ + \ \mathrm{C_6H_{12}O_6}(aq)$$

    Rate = $k[C_{12}H_{22}O_{11}]$

    In neutral solution, $k = 2.1 \times 10^{-11}$/s at 27 °C. (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas, $C_6H_{12}O_6$, but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is 1.36×10^5 at 27 °C. What are the concentrations of glucose, fructose, and sucrose after a 0.150 M aqueous solution of sucrose has reached equilibrium? Remember that the activity of a solvent (the effective concentration) is 1. **Check Answer:** [48]

48. The density of trifluoroacetic acid vapour was determined at 118.1 °C and 468.5 torr, and found to be 2.784 g/L. Calculate K_c for the association of the acid shown in the figure below.



49. Liquid N_2O_3 is dark blue at low temperatures, but the colour fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of K_P = 1.91 has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of N_2O_3(*g*), NO_2(*g*), and NO(*g*).
    Check Answer: [49]

50. A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 M; H_2, 0.50 M; and NH_3, 0.25 M. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 M?

51. A 0.010 M solution of the weak acid HA has an osmotic pressure (see chapter on solutions and colloids) of 0.293 atm at 25 °C. A 0.010 M solution of the weak acid HB has an osmotic pressure of 0.345 atm

under the same conditions.

a. Which acid has the larger equilibrium constant for ionization HA $[\mathrm{HA}(aq) \rightleftharpoons \mathrm{A}^-(aq) + \mathrm{H}^+(aq)]$ or HB $[\mathrm{HB}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{B}^-(aq)]$?
b. What are the equilibrium constants for the ionization of these acids?

(Hint: Remember that each solution contains three dissolved species: the weak acid (HA or HB), the conjugate base (A^- or B^-), and the hydrogen ion (H^+). Remember that osmotic pressure (like all colligative properties) is related to the total number of solute particles. Specifically for osmotic pressure, those concentrations are described by molarities.) **Check Answer:** [50]

17.6 Precipitation and Dissolution

1. Complete the changes in concentrations for each of the following reactions in the table below:

a.	$AgI_{(s)}$	→	$Ag^+_{(aq)}$	$+ I^-_{(aq)}$	
			x	______	
b.	$CaCO_{3(s)}$	→	$Ca^{2+}_{(aq)}$	$+ CO_3^{2-}{}_{(aq)}$	
			______	x	
c.	$Mg(OH)_{2(s)}$	→	$Mg^{2+}_{(aq)}$	$+ 2\ OH^-_{(aq)}$	
			x	______	
d.	$Mg_3(PO_4)_{2(s)}$	→	$3\ Mg^{2+}_{(aq)}$	$+ 2\ PO_4^{3-}{}_{(aq)}$	
			______	2x	
e.	$Ca_5(PO_4)_3OH_{(s)}$	→	$5\ Ca^{2+}_{(aq)}$	$+ 3\ PO_4^{3-}{}_{(aq)}$	$+ OH^-_{(aq)}$
			______	______	x

Check Answer: [51]

2. Complete the changes in concentrations for each of the following reactions in the table below:

a.	$BaSO_{4\,(s)}$	→	$Ba^{2+}{}_{(aq)}$	$+\ SO_4{}^{2-}{}_{(aq)}$	
			x	______	
b.	$Ag_2SO_{4\,(s)}$	→	$2\ Ag^{+}{}_{(aq)}$	$+\ SO_4{}^{2-}{}_{(aq)}$	
			______	x	
c.	$Al(OH)_{3\,(s)}$	→	$Al^{3+}{}_{(aq)}$	$+\ 3\ OH^{-}{}_{(aq)}$	
			x	______	
d.	$Pb(OH)Cl_{\,(s)}$	→	$Pb^{2+}{}_{(aq)}$	$+\ OH^{-}{}_{(aq)}$	$+\ Cl^{-}{}_{(aq)}$
			______	x	______
e.	$Ca_3(AsO_4)_{2\,(s)}$	→	$3\ Ca^{2+}{}_{(aq)}$	$+\ 2\ AsO_4{}^{3-}{}_{(aq)}$	
			3x	______	

3. How do the concentrations of Ag^+ and $CrO_4{}^{2-}$ in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain. **Check Answer:** [52]
4. How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS?
5. What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised? **Check Answer:** [53]
6. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: $CoSO_3$, CuI, $PbCO_3$, $PbCl_2$, Tl_2S, $KClO_4$?
7. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl, $BaSO_4$, CaF_2, Hg_2I_2, $MnCO_3$, ZnS, PbS? **Check Answer:** [54]
8. Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:
    a. $PbCl_2$
    b. Ag_2S
    c. $Sr_3(PO_4)_2$
    d. $SrSO_4$
9. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:
    a. LaF_3
    b. $CaCO_3$

   c. Ag_2SO_4
   d. $Pb(OH)_2$

   Check Answer: [55]

10. The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.
    a. $BaSiF_6$, 0.026 g/100 mL (contains SiF_6^{2-} ions)
    b. $Ce(IO_3)_4$, 1.5×10^{-2} g/100 mL
    c. $Gd_2(SO_4)_3$, 3.98 g/100 mL
    d. $(NH_4)_2PtBr_6$, 0.59 g/100 mL (contains $PtBr_6^{2-}$ ions)
11. The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.
    a. $BaSeO_4$, 0.0118 g/100 mL
    b. $Ba(BrO_3)_2{\cdot}H_2O$, 0.30 g/100 mL
    c. $NH_4MgAsO_4{\cdot}6H_2O$, 0.038 g/100 mL
    d. $La_2(MoO_4)_3$, 0.00179 g/100 mL

    Check Answer: [56]
12. Use solubility products and predict which of the following salts is the most soluble, in terms of moles per litre, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.
13. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:
    a. $KHC_4H_4O_6$
    b. PbI_2
    c. $Ag_4[Fe(CN)_6]$, a salt containing the $Fe(CN)_4^-$ ion
    d. Hg_2I_2

    Check Answer: [57]
14. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:
    a. Ag_2SO_4
    b. $PbBr_2$
    c. AgI
    d. $CaC_2O_4{\cdot}H_2O$
15. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.
    a. $AgCl(s)$ in 0.025 M NaCl

   b. CaF_2(*s*) in 0.00133 *M* KF
   c. Ag_2SO_4(*s*) in 0.500 L of a solution containing 19.50 g of K_2SO_4
   d. $Zn(OH)_2$(*s*) in a solution buffered at a pH of 11.45
   Check Answer: [58]

16. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.
   a. TlCl(*s*) in 1.250 *M* HCl
   b. PbI_2(*s*) in 0.0355 *M* CaI_2
   c. Ag_2CrO_4(*s*) in 0.225 L of a solution containing 0.856 g of K_2CrO_4
   d. $Cd(OH)_2$(*s*) in a solution buffered at a pH of 10.995
17. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.
   a. TlCl(*s*) in 0.025 *M* $TlNO_3$
   b. BaF_2(*s*) in 0.0313 *M* KF
   c. MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $Mg(NO_3)_2$
   d. $Ca(OH)_2$(*s*) in an unbuffered solution initially with a pH of 12.700
   Check Answer: [59]
18. Calculate the solubility of aluminum hydroxide, $Al(OH)_3$, in a solution buffered at pH 11.00.
19. Refer to Appendix K for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per litre and which is most soluble in grams per litre. **Check Answer:** [60]
20. Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract (Figure 17.6c). This use of $BaSO_4$ is possible because of its low solubility. Calculate the molar solubility of $BaSO_4$ and the mass of barium present in 1.00 L of water saturated with $BaSO_4$.
21. Public Health Service standards for drinking water set a maximum of 250 mg/L (2.60×10^{-3} *M*) of SO_4^{2-} because of its cathartic action (it is a laxative). Does natural water that is saturated with $CaSO_4$ ("gyp" water) as a result or passing through soil containing gypsum, $CaSO_4{\cdot}2H_2O$, meet these standards? What is SO_4^{2-} in such water? **Check Answer:** [61]
22. Perform the following calculations:
   a. Calculate $[Ag^+]$ in a saturated aqueous solution of AgBr.
   b. What will $[Ag^+]$ be when enough KBr has been added to make $[Br^-] = 0.050$ *M*?
   c. What will $[Br^-]$ be when enough $AgNO_3$ has been added to make $[Ag^+] = 0.020$ *M*?
23. The solubility product of $CaSO_4{\cdot}2H_2O$ is 2.4×10^{-5}. What mass of this salt will dissolve in 1.0 L of 0.010 *M* SO_4^{2-}? **Check Answer:** [62]
24. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a

saturated solution of each of the following (see Appendix K for solubility products).

a. $TlCl$
b. BaF_2
c. Ag_2CrO_4
d. $CaC_2O_4{\cdot}H_2O$
e. the mineral anglesite, $PbSO_4$

25. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Appendix K for solubility products):

a. AgI
b. Ag_2SO_4
c. $Mn(OH)_2$
d. $Sr(OH)_2{\cdot}8H_2O$
e. the mineral brucite, $Mg(OH)_2$

Check Answer: [63]

26. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

a. $AgBr$: $[Ag^+] = 5.7 \times 10^{-7}\,M$, $[Br^-] = 5.7 \times 10^{-7}\,M$
b. $CaCO_3$: $[Ca^{2+}] = 5.3 \times 10^{-3}\,M$, $[CO_3{}^{2-}] = 9.0 \times 10^{-7}\,M$
c. PbF_2: $[Pb^{2+}] = 2.1 \times 10^{-3}\,M$, $[F^-] = 4.2 \times 10^{-3}\,M$
d. Ag_2CrO_4: $[Ag^+] = 5.3 \times 10^{-5}\,M$, $3.2 \times 10^{-3}\,M$
e. InF_3: $[In^{3+}] = 2.3 \times 10^{-3}\,M$, $[F^-] = 7.0 \times 10^{-3}\,M$

27. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

a. $TlCl$: $[Tl^+] = 1.21 \times 10^{-2}\,M$, $[Cl^-] = 1.2 \times 10^{-2}\,M$
b. $Ce(IO_3)_4$: $[Ce^{4+}] = 1.8 \times 10^{-4}\,M$, $[IO_3{}^-] = 2.6 \times 10^{-13}\,M$
c. $Gd_2(SO_4)_3$: $[Gd^{3+}] = 0.132\,M$, $[SO_4{}^{2-}] = 0.198\,M$
d. Ag_2SO_4: $[Ag^+] = 2.40 \times 10^{-2}\,M$, $[SO_4{}^{2-}] = 2.05 \times 10^{-2}\,M$
e. $BaSO_4$: $[Ba^{2+}] = 0.500\,M$, $[SO_4{}^{2-}] = 2.16 \times 10^{-10}\,M$

Check Answer: [64]

28. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Appendix K for K_{sp} values.)

a. $KClO_4$: $[K^+] = 0.01\,M$, $[ClO_4{}^-] = 0.01\,M$
b. K_2PtCl_6: $[K^+] = 0.01\,M$, $[PtCl_6{}^{2-}] = 0.01\,M$
c. PbI_2: $[Pb^{2+}] = 0.003\,M$, $[I^-] = 1.3 \times 10^{-3}\,M$
d. Ag_2S: $[Ag^+] = 1 \times 10^{-10}\,M$, $[S^{2-}] = 1 \times 10^{-13}\,M$

29. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Appendix K for K_{sp} values.)

   a. $CaCO_3$: $[Ca^{2+}] = 0.003\ M$, $[CO_3^{2-}] = 0.003\ M$
   b. $Co(OH)_2$: $[Co^{2+}] = 0.01\ M$, $[OH^-] = 1 \times 10^{-7} M$
   c. $CaHPO_4$: $[Ca^{2+}] = 0.01\ M$, $[HPO_4^{2-}] = 2 \times 10^{-6} M$
   d. $Pb_3(PO_4)_2$: $[Pb^{2+}] = 0.01\ M$, $[PO_4^{3-}] = 1 \times 10^{-13} M$

   Check Answer: [65]

30. Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 M in Cl^-.
31. Calculate the concentration of sulfate ion when $BaSO_4$ just begins to precipitate from a solution that is 0.0758 M in Ba^{2+}. **Check Answer:** [66]
32. Calculate the concentration of Sr^{2+} when SrF_2 starts to precipitate from a solution that is 0.0025 M in F^-.
33. Calculate the concentration of PO_4^{3-} when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 M in Ag^+. **Check Answer:** [67]
34. Calculate the concentration of F^- required to begin precipitation of CaF_2 in a solution that is 0.010 M in Ca^{2+}.
35. Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is $2.50 \times 10^{-6} M$ in CO_3^{2-}. **Check Answer:** [68]
36. What $[Ag^+]$ is required to reduce $[CO_3^{2-}]$ to $8.2 \times 10^{-4} M$ by precipitation of Ag_2CO_3?
37. What $[F^-]$ is required to reduce $[Ca^{2+}]$ to $1.0 \times 10^{-4} M$ by precipitation of CaF_2? **Check Answer:** [69]
38. A volume of 0.800 L of a 2×10^{-4}–M $Ba(NO_3)_2$ solution is added to 0.200 L of $5 \times 10^{-4} M$ Li_2SO_4. Does $BaSO_4$ precipitate? Explain your answer.
39. Perform these calculations for nickel(II) carbonate.
   a. With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ ($K_{sp} = 1.36 \times 10^{-7}$).
   b. If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ ($K_{sp} = 1.0 \times 10^{-12}$), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.

   Check Answer: [70]
40. Iron concentrations greater than $5.4 \times 10^{-6} M$ in water used for laundry purposes can cause staining. What $[OH^-]$ is required to reduce $[Fe^{2+}]$ to this level by precipitation of $Fe(OH)_2$?
41. A solution is 0.010 M in both Cu^{2+} and Cd^{2+}. What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide? **Check Answer:** [71]
42. A solution is 0.15 M in both Pb^{2+} and Ag^+. If Cl^- is added to this solution, what is $[Ag^+]$ when $PbCl_2$ begins to precipitate?
43. What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 M with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in Appendix K.)

   a. Hg_2^{2+} and Cu^{2+}
   b. SO_4^{2-} and Cl^-
   c. Hg^{2+} and Co^{2+}
   d. Zn^{2+} and Sr^{2+}
   e. Ba^{2+} and Mg^{2+}
   f. CO_3^{2-} and OH^-

   Check Answer: [72]

44. A solution contains 1.0×10^{-5} mol of KBr and 0.10 mol of KCl per litre. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?
45. A solution contains 1.0×10^{-2} mol of KI and 0.10 mol of KCl per litre. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl? **Check Answer:** [73]
46. The calcium ions in human blood serum are necessary for coagulation. Potassium oxalate, $K_2C_2O_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $CaC_2O_4{\cdot}H_2O$. It is necessary to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $K_2C_2O_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)
47. About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form? **Check Answer:** [74]
48. The pH of normal urine is 6.30, and the total phosphate concentration $[PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$ is 0.020 M. What is the minimum concentration of Ca^{2+} necessary to induce kidney stone formation?
49. Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

$$\text{Mg}^{2+}(aq) + \text{Ca(OH)}_2(aq) \longrightarrow \text{Mg(OH)}_2(s) + \text{Ca}^{2+}(aq)$$
$$\text{Mg(OH)}_2(s) + 2\text{HCl}(aq) \longrightarrow \text{MgCl}_2(s) + 2\text{H}_2\text{O}(l)$$
$$\text{MgCl}_2(l) \xrightarrow{\text{electrolysis}} \text{Mg}(s) + \text{Cl}_2(g)$$

   Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $Mg^{2+}(aq)$ by mass. What mass, in kilograms, of $Ca(OH)_2$ is required to precipitate 99.9% of the magnesium in 1.00×10^3 L of sea water? **Check Answer:** [75]
50. Hydrogen sulfide is bubbled into a solution that is 0.10 M in both Pb^{2+} and Fe^{2+} and 0.30 M in HCl. After the solution has come to equilibrium it is saturated with H_2S ($[H_2S] = 0.10$ M). What

concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H_2S we can use the equilibrium:

$$\mathrm{H_2S}(aq) + \mathrm{2H_2O}(l) \rightleftharpoons \mathrm{2H_3O^+}(aq) + \mathrm{S^{2-}}(aq) \qquad K = 1.0 \times 10^{-26}$$

(Hint: The $[H_3O^+]$ changes as metal sulfides precipitate.)

51. Perform the following calculations involving concentrations of iodate ions:
    a. The iodate ion concentration of a saturated solution of $La(IO_3)_3$ was found to be 3.1×10^{-3} mol/L. Find the K_{sp}.
    b. Find the concentration of iodate ions in a saturated solution of $Cu(IO_3)_2$ ($K_{sp} = 7.4 \times 10^{-8}$).
    Check Answer: [76]
52. Calculate the molar solubility of AgBr in 0.035 *M* NaBr ($K_{sp} = 5 \times 10^{-13}$).
53. How many grams of $Pb(OH)_2$ will dissolve in 500 mL of a 0.050-*M* $PbCl_2$ solution ($K_{sp} = 1.2 \times 10^{-15}$)? **Check Answer:** [77]
54. How many grams of Milk of Magnesia, $Mg(OH)_2$ (*s*) (58.3 g/mol), would be soluble in 200 mL of water. $K_{sp} = 7.1 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. ($K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$)
55. Two hypothetical salts, LM_2 and LQ, have the same molar solubility in H_2O. If K_{sp} for LM_2 is 3.20×10^{-5}, what is the K_{sp} value for LQ? **Check Answer:** [78]
56. Which of the following carbonates will form first? Which of the following will form last? Explain.
    a. $\mathrm{MgCO_3} \qquad K_{sp} = 3.5 \times 10^{-8}$
    b. $\mathrm{CaCO_3} \qquad K_{sp} = 4.2 \times 10^{-7}$
    c. $\mathrm{SrCO_3} \qquad K_{sp} = 3.9 \times 10^{-9}$
    d. $\mathrm{BaCO_3} \qquad K_{sp} = 4.4 \times 10^{-5}$
    e. $\mathrm{MnCO_3} \qquad K_{sp} = 5.1 \times 10^{-9}$
    Check Answer: [79]
57. How many grams of $Zn(CN)_2$(*s*) (117.44 g/mol) would be soluble in 100 mL of H_2O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $Zn(CN)_2$(*s*) is 3.0×10^{-16}.

17.7 Relative Strengths of Acids and Bases

1. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.
2. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.
   Check Answer: [80]
3. Use this list of important industrial compounds (and Figure 17.7c) to answer the following questions regarding: CaO, $Ca(OH)_2$, CH_3CO_2H, CO_2, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4,

NH_3, NaOH, Na_2CO_3.
   a. Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
   b. List those compounds in (a) that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
   c. List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.
4. The odour of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid. **Check Answer:** [81]
5. Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.
6. Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3. **Check Answer:** [82]
7. Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.
8. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs. **Check Answer:** [83]
9. Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.
10. What is the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$. **Check Answer:** [84]
11. What is the ionization constant at 25 °C for the weak acid $(CH_3)_2NH_2^+$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 5.9 \times 10^{-4}$?
12. Which base, CH_3NH_2 or $(CH_3)_2NH$, is the stronger base? Which conjugate acid, $(CH_3)_2NH_2^+$ or $(CH_3)_2NH$, is the stronger acid? **Check Answer:** [85]
13. Which is the stronger acid, NH_4^+ or HBrO?
14. Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$? **Check Answer:** [86]
15. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.
   a. H_2O or HF
   b. $B(OH)_3$ or $Al(OH)_3$
   c. HSO_3^- or HSO_4^-
   d. NH_3 or H_2S
   e. H_2O or H_2Te
16. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

   a. HSO_4^- or $HSeO_4^-$
   b. NH_3 or H_2O
   c. PH_3 or HI
   d. NH_3 or PH_3
   e. H_2S or HBr
   Check Answer: [87]
17. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.
   a. acidity: HCl, HBr, HI
   b. basicity: H_2O, OH^-, H^-, Cl^-
   c. basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$).
   d. acidity: HF, H_2O, NH_3, CH_4
18. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.
   a. acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$
   b. basicity: BrO_2^-, ClO_2^-, IO_2^-
   c. acidity: HOCl, HOBr, HOI
   d. acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$
   e. basicity: NH_2^-, HS^-, HTe^-, PH_2^-
   f. basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-
   Check Answer: [88]
19. Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base? See Table 17.7b.
20. The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-M aqueous solution of $C_6H_4OH(CO_2H)$. **Check Answer:** [89]
21. What do we represent when we write:
$$\text{CH}_3\text{CO}_2\text{H}(aq) \ + \ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) \ + \ \text{CH}_3\text{CO}_2{}^-(aq)?$$
22. Explain why equilibrium calculations are not necessary to determine ionic concentrations in solutions of certain strong electrolytes such as NaOH and HCl. Under what conditions are equilibrium calculations necessary as part of the determination of the concentrations of all ions of some other strong electrolytes in solution? **Check Answer:** [90]
23. Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.
24. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid? **Check Answer:** [91]

25. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?
26. Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water (Hint: Use LeChâtelier's principle.)?
    a. addition of NaOH
    b. addition of HCl
    c. addition of NH_4Cl
    Check Answer: [92]
27. Which of the following will increase the percent of HF that is converted to the fluoride ion in water?
    a. addition of NaOH
    b. addition of HCl
    c. addition of NaF
28. What is the effect on the concentrations of NO_2^-, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:
    a. HCl
    b. HNO_2
    c. NaOH
    d. NaCl
    e. KNO
    The equation for the equilibrium is:
    $$\mathrm{NO_2}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH}^-(aq)$$
    Check Answer: [93]
29. What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?
    a. HCl
    b. KF
    c. NaCl
    d. KOH
    e. HF
    The equation for the equilibrium is: $\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{F}^-(aq)$
30. Why is the hydronium ion concentration in a solution that is 0.10 M in HCl and 0.10 M in HCOOH determined by the concentration of HCl? **Check Answer:** [94]
31. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.
    a. CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3} M$;
    $[CH_3CO_2^-] = 1.34 \times 10^{-3} M$;
    $[CH_3CO_2H] = 9.866 \times 10^{-2} M$;

b. ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*;
$[HClO] = 2.38 \times 10^{-5}$ *M*;
$[ClO^-] = 0.273$ *M*;

c. HCO_2H: $[HCO_2H] = 0.524$ *M*;
$[H_3O^+] = 9.8 \times 10^{-3}$ *M*;
$[HCO_2^-] = 9.8 \times 10^{-3}$ *M*;

d. $C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233$ *M*;
$[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;
$[H_3O^+] = 2.3 \times 10^{-3}$ *M*

32. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

a. NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;
$[NH_4^+] = 3.1 \times 10^{-3}$ *M*;
$[NH_3] = 0.533$ *M*;

b. HNO_2: $[H_3O^+] = 0.011$ *M*;
$[NO_2^-] = 0.0438$ *M*;
$[HNO_2] = 1.07$ *M*;

c. $(CH_3)_3N$: $[(CH_3)_3N] = 0.25$ *M*;
$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}$ *M*;
$[OH^-] = 4.3 \times 10^{-3}$ *M*;

d. NH_4^+: $[NH_4^+] = 0.100$ *M*;
$[NH_3] = 7.5 \times 10^{-6}$ *M*;
$[H_3O^+] = 7.5 \times 10^{-6}$ *M*
Check Answer: [95]

33. Determine K_b for the nitrite ion, NO_2^-. In a 0.10-*M* solution this base is 0.0015% ionized.
34. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized. **Check Answer:** [96]
35. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

a. F^-
b. NH_4^+
c. AsO_4^{3-}
d. $(CH_3)_2NH_2^+$

   e. NO_2^-
   f. $HC_2O_4^-$ (as a base)
36. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:
   a. HTe^- (as a base)
   b. $(CH_3)_3NH^+$
   c. $HAsO_4^{3-}$ (as a base)
   d. HO_2^- (as a base)
   e. $C_6H_5NH_3^+$
   f. HSO_3^- (as a base)

   Check Answer: [97]
37. For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?
   a. 3×10^{-8} *M* HNO_3
   b. 0.10 g HCl in 1.0 L of solution
   c. 0.00080 g NaOH in 0.50 L of solution
   d. 1×10^{-7} *M* $Ca(OH)_2$
   e. 0.0245 *M* KNO_3
38. Even though both NH_3 and $C_6H_5NH_2$ are weak bases, NH_3 is a much stronger acid than $C_6H_5NH_2$. Which of the following is correct at equilibrium for a solution that is initially 0.10 *M* in NH_3 and 0.10 *M* in $C_6H_5NH_2$?
   a. $[OH^-] = [NH_4^+]$
   b. $[NH_4^+] = [C_6H_5NH_3^+]$
   c. $[OH^-] = [C_6H_5NH_3^+]$
   d. $[NH_3] = [C_6H_5NH_2]$
   e. both a and b are correct

   Check Answer: [98]
39. Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.25 *M* in HCO_2H and 0.10 *M* in HClO.
40. Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.134 *M* in HNO_2 and 0.120 *M* in HBrO. **Check Answer:** [99]
41. Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 *M* in CH_3NH_2 and 0.10 *M* in C_5H_5N ($K_b = 1.7 \times 10^{-9}$).
42. Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.115 *M* in NH_3 and 0.100 *M* in $C_6H_5NH_2$. **Check Answer:** [100]
43. Using the K_a value of 1.4×10^{-5}, place $Al(H_2O)_6^{3+}$ in the correct location in Figure 17.7c.

44. Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected. Ionization constants can be found in Appendix I and Appendix J.
    a. 0.0092 *M* HClO, a weak acid
    b. 0.0784 *M* $C_6H_5NH_2$, a weak base
    c. 0.0810 *M* HCN, a weak acid
    d. 0.11 *M* $(CH_3)_3N$, a weak base
    e. 0.120 *M* $FeH_2O_6{}^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$
    Check Answer: [101]
45. Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the hydronium ion concentration in a 0.698-*M* solution of $C_2H_5CO_2H$?
46. White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH? **Check Answer:** [102]
47. The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?
48. Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_1 = 7 \times 10^{-7}$, $K_2 = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine? **Check Answer:** [103]
49. The pH of a 0.20-*M* solution of HF is 1.92. Determine K_a for HF from these data.
50. The pH of a 0.15-*M* solution of $HSO_4{}^-$ is 1.43. Determine K_a for $HSO_4{}^-$ from these data. **Check Answer:** [104]
51. The pH of a 0.10-*M* solution of caffeine is 11.16. Determine K_b for caffeine from these data:
    $$C_8H_{10}N_4O_2(aq) + H_2O(l) \leftrightharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$
52. The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data. **Check Answer:** [105]

17.8 Real World Examples of Equilibria

1. A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?
2. Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$. **Check Answer:** [106]
3. Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of $Zn(CN)_4{}^{2-}$.
4. Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3. **Check Answer:** [107]
5. Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^-.

6. Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 M CN^-. **Check Answer:** [108]
7. Calculate the Co^{2+} equilibrium concentration when 0.100 mole of $[Co(NH_3)_6](NO_3)_2$ is added to a solution with 0.025 M NH_3. Assume the volume is 1.00 L.
8. The equilibrium constant for the reaction $\text{Hg}^{2+}(aq) + 2\text{Cl}^-(aq) \leftrightharpoons \text{HgCl}_2(aq)$ is 1.6×10^{13}. Is $HgCl_2$ a strong electrolyte or a weak electrolyte? What are the concentrations of Hg^{2+} and Cl^- in a 0.015-M solution of $HgCl_2$? **Check Answer:** [109]
9. Calculate the molar solubility of $Sn(OH)_2$ in a buffer solution containing equal concentrations of NH_3 and NH_4^+.
10. Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 M NH_3 and 0.400 M NH_4^+. **Check Answer:** [110]
11. What is the molar solubility of CaF_2 in a 0.100-M solution of HF? K_a for HF = 7.2×10^{-4}.
12. What is the molar solubility of $BaSO_4$ in a 0.250-M solution of $NaHSO_4$? K_a for HSO_4^- = 1.2×10^{-2}. **Check Answer:** [111]
13. What is the molar solubility of $Tl(OH)_3$ in a 0.10-M solution of NH_3?
14. What is the molar solubility of $Pb(OH)_2$ in a 0.138-M solution of CH_3NH_2? **Check Answer:** [112]
15. A solution of 0.075 M $CoBr_2$ is saturated with H_2S ($[H_2S] = 0.10$ M). What is the minimum pH at which CoS begins to precipitate?
$$\text{CoS}(s) \leftrightharpoons \text{Co}^{2+}(aq) + \text{S}^{2-}(aq) \qquad K_{\text{sp}} = 4.5 \times 10^{-27}$$
$$\text{H}_2\text{S}(aq) + 2\text{H}_2\text{O}(l) \leftrightharpoons 2\text{H}_3\text{O}^+(aq) + \text{S}^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$
16. A 0.125-M solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S] = 0.10$ M). At what pH does MnS begin to precipitate?
$$\text{MnS}(s) \rightleftharpoons \text{Mn}^{2+}(aq) + \text{S}^{2-}(aq) \qquad K_{\text{sp}} = 4.3 \times 10^{-22}$$
$$\text{H}_2\text{S}(aq) + 2\text{H}_2\text{O}(l) \rightleftharpoons 2\text{H}_3\text{O}^+(aq) + \text{S}^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$
Check Answer: [113]
17. Calculate the molar solubility of BaF_2 in a buffer solution containing 0.20 M HF and 0.20 M NaF.
18. Calculate the molar solubility of $CdCO_3$ in a buffer solution containing 0.115 M Na_2CO_3 and 0.120 M $NaHCO_3$ **Check Answer:** [114]
19. To a 0.10-M solution of $Pb(NO_3)_2$ is added enough HF(g) to make [HF] = 0.10 M.
    a. Does PbF_2 precipitate from this solution? Show the calculations that support your conclusion.
    b. What is the minimum pH at which PbF_2 precipitates?
20. Calculate the concentration of Cd^{2+} resulting from the dissolution of $CdCO_3$ in a solution that is 0.010 M in H_2CO_3. **Check Answer:** [115]
21. Both AgCl and AgI dissolve in NH_3.
    a. What mass of AgI dissolves in 1.0 L of 1.0 M NH_3?
    b. What mass of AgCl dissolves in 1.0 L of 1.0 M NH_3?
22. Calculate the volume of 1.50 M CH_3CO_2H required to dissolve a precipitate composed of 350 mg each

of $CaCO_3$, $SrCO_3$, and $BaCO_3$. **Check Answer:** [116]

23. Even though $Ca(OH)_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of $Ca(OH)_2$?
24. What mass of NaCN must be added to 1 L of 0.010 M $Mg(NO_3)_2$ in order to produce the first trace of $Mg(OH)_2$? **Check Answer:** [117]
25. Magnesium hydroxide and magnesium citrate function as mild laxatives when they reach the small intestine. Why do magnesium hydroxide and magnesium citrate, two very different substances, have the same effect in your small intestine. (Hint: The contents of the small intestine are basic.)
26. The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.
    Solve the following problem:

    $$\mathrm{MgF_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\mathrm{F^-}(aq)$$

    In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is $1.21 \times 10^{-3} M$. The equilibrium is represented by the preceding equation.
    1. Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.
    2. Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
    3. Predict whether a precipitate of MgF_2 will form when 100.0 mL of a 3.00×10^{-3}–M solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a 2.00×10^{-3}–M solution of NaF at 18 °C. Show the calculations to support your prediction.
    4. At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is $1.17 \times 10^{-3} M$. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.
       Check Answer: [118]
27. Which of the following compounds, when dissolved in a 0.01-M solution of $HClO_4$, has a solubility greater than in pure water: CuCl, $CaCO_3$, MnS, $PbBr_2$, CaF_2? Explain your answer.
28. Which of the following compounds, when dissolved in a 0.01-M solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_3$, ZnS, PbI_2? Explain your answer. **Check Answer:** [119]
29. What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ and water at equilibrium?
    1. $MgCl_2$
    2. KOH
    3. $HClO_4$
    4. $NaNO_3$

   e. $Mg(OH)_2$

30. What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and HPO_4^{-} when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?
   a. $CaCl_2$
   b. HCl
   c. $KClO_4$
   d. NaOH
   e. $CaHPO_4$

   Check Answer: [120]
31. Identify all chemical species present in an aqueous solution of $Ca_3(PO_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the PO_4^{3-} ion is a weak base.)
32. A volume of 50 mL of 1.8 M NH_3 is mixed with an equal volume of a solution containing 0.95 g of $MgCl_2$. What mass of NH_4Cl must be added to the resulting solution to prevent the precipitation of $Mg(OH)_2$? **Check Answer:** [121]

Attribution & References

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Notes

1. The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.
2. $$\text{rate} = +\frac{1}{2}\frac{\Delta[\text{CIF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\text{F}_2]}{\Delta t}$$
3. (a) average rate, 0 – 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 12 – 18 s = 0.0225 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.0500 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.0250 mol L^{-1} s^{-1}
4. The reaction can proceed in both the forward and reverse directions.

5. When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.
6. The concept of equilibrium does not imply equal concentrations, though it is possible.
7. Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.
8. (a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) $K_c = \frac{1}{[Pb^{2+}][Cl^-]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).
9. Since $K_c = \frac{[C_6H_6]}{[C_2H_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.
10. $K_c > 1$
11. (a) $Q_c = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$; (b) $Q_c = \frac{[NO]^2}{[N_2][O_2]}$; (c) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (d) $Q_c = [SO_2]$; (e) $Q_c = \frac{1}{[P_4][O_2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br_2]}$; (g) $Q_c = \frac{[CO_2]}{[CH_4][O_2]^2}$; (h) $Q_c = [H_2O]^5$
12. (a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left
13. The system will shift toward the reactants to reach equilibrium.
14. (a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$
15. $K_P = P_{H_2O} = 0.042$.
16. $Q_c = \frac{[NH_4{}^+][OH^-]}{[NH_3]}$
17. The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.
18. The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.
19. No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.
20. Add N_2; add H_2; decrease the container volume; heat the mixture.
21. (a) $K_c = \frac{[CO][H_2]}{[H_2O]}$; (b) $[H_2O]$ no change, [CO] no change, $[H_2]$ no change; (c) $[H_2O]$ decreases, [CO] decreases, $[H_2]$ decreases; (d) $[H_2O]$ increases, [CO] increases, $[H_2]$ decreases; (f) $[H_2O]$ decreases, [CO] increases,

$[H_2]$ increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

22. Only (b)
23. Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(*s*).
24. (a)
25. $K_c = \frac{[C]^2}{[A][B]^2}$. [A] = 0.1 M, [B] = 0.1 M, [C] = 1 M; and [A] = 0.01, [B] = 0.250, [C] = 0.791.
26. $K_c = 6.00 \times 10^{-2}$
27. $K_c = 0.50$
28. The equilibrium equation is $K_P = 1.9 \times 10^3$
29. $K_P = 3.06$
30. (a) $-2x$, $2x$, $-0.250\ M$, $0.250\ M$; (b) $4x$, $-2x$, $-6x$, $0.32\ M$, $-0.16\ M$, $-0.48\ M$; (c) $-2x$, $3x$, −50 torr, 75 torr; (d) x, $-x$, $-3x$, 5 atm, −5 atm, −15 atm; (e) x, $1.03 \times 10^{-4} M$; (f) x, 0.1 atm.
31. Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.
32. $[NH_3] = 9.1 \times 10^{-2} M$
33. $P_{BrCl} = 4.9 \times 10^{-2}$ atm
34. $[CO] = 2.0 \times 10^{-4} M$
35. $P_{H_2O} = 3.64 \times 10^{-3}$ atm
36. Calculate Q based on the calculated concentrations and see if it is equal to K_c. Because Q does equal 4.32, the system must be at equilibrium.
37. (a) $[NO_2] = 1.17 \times 10^{-3} M$; $[N_2O_4] = 0.128\ M$ (b) Percent error $= \frac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$. The change in concentration of N_2O_4 is far less than the 5% maximum allowed.
38. (a) $[H_2S] = 0.810$ atm ; $[H_2] = 0.014$ atm ; $[S_2] = 0.0072$ atm (b) The $2x$ is dropped from the equilibrium calculation because 0.014 is negligible when subtracted from 0.824. The percent error associated with ignoring $2x$ is $\frac{0.014}{0.824} \times 100\% = 1.7\%$, which is less than allowed by the "5% test." The error is, indeed, negligible.
39. $[PCl_3] = 1.80\ M$; $[PC_3] = 0.195\ M$; $[PCl_3] = 0.195\ M$.
40. $[NO_2] = 0.19\ M$; $[NO] = 0.0070\ M$; $[O_2] = 0.0035\ M$
41. $P_{O_3} = 4.9 \times 10^{-26}$ atm
42. 507 g
43. 330 g
44. (a) Both gases must increase in pressure. (b) $P_{N_2O_4} = 8.0$ atm and $P_{NO_2} = 1.0$ atm
45. (a) 0.33 mol. (b) $[CO]^2 = 0.50\ M$ Added H_2 forms some water to compensate for the removal of water vapour and as a result of a shift to the left after H_2 is added.
46. $P_{H_2} = 8.64 \times 10^{-11}$ atm $P_{O_2} = 0.250$ atm $P_{H_2O} = 0.500$ atm

47. (a) $K_c = \dfrac{[\mathrm{NH_3}]^4[\mathrm{O_2}]^7}{[\mathrm{NO_2}]^4[\mathrm{H_2O}]^6}$. (b) [$NH_3$] must increase for Q_c to reach K_c. (c) That decrease in pressure would decrease [NO_2]. (d) $P_{\mathrm{O_2}} = 49\ \text{torr}$

48. [fructose] = 0.15 *M*

49. $P_{\mathrm{N_2O_3}} = 1.90\ \text{atm and}\ P_{\mathrm{NO}} = P_{\mathrm{NO_2}} = 1.90\ \text{atm}$

50. (a) HB ionizes to a greater degree and has the larger K_c. (b) K_c(HA) = 5 × 10^{-4} K_c(HB) = 3 × 10^{-3}

51. (a) $\mathrm{AgI}(s) \rightleftharpoons \quad \mathrm{Ag}^{+}(aq) \quad + \quad \mathrm{I}^{-}(aq)$ (b)

$$x \qquad\qquad \underline{x}$$

$$\mathrm{CaCO_3}(s) \rightleftharpoons \quad \mathrm{Ca}^{2+}(aq) \quad + \quad \mathrm{CO_3}^{2-}(aq)$$ (c)

$$\underline{x} \qquad\qquad x$$

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \quad \mathrm{Mg}^{2+}(aq) \quad + \quad 2\mathrm{OH}^{-}(aq)$$ (d)

$$x \qquad\qquad \underline{2x}$$

$$\mathrm{Mg_3(PO_4)_2}(s) \rightleftharpoons \quad 3\mathrm{Mg}^{2+}(aq) \quad + \quad 2\mathrm{PO_4}^{3-}(aq)$$ (e)

$$\underline{3x} \qquad\qquad 2x$$

$$\mathrm{Ca_5(PO_4)_3OH}(s) \rightleftharpoons \quad 5\mathrm{Ca}^{2+}(aq) \quad + \quad 3\mathrm{PO_4}^{3-}(aq) \quad + \quad \mathrm{OH}^{-}(aq)$$

$$\underline{5x} \qquad\qquad \underline{3x} \qquad\qquad x$$

52. There is no change. A solid has an activity of 1 whether there is a little or a lot.

53. The solubility of silver bromide at the new temperature must be known. Normally the solubility increases and some of the solid silver bromide will dissolve.

54. CaF_2, $MnCO_3$, and ZnS

55. (a) $\mathrm{LaF_3}(s) \rightleftharpoons \mathrm{La}^{3+}(aq) + 3\mathrm{F}^{-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{La}^{3+}][\mathrm{F}^{-}]^3$; (b) $\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{CO_3}^{2-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{CO_3}^{2-}]$; (c) $\mathrm{Ag_2SO_4}(s) \rightleftharpoons 2\mathrm{Ag}^{+}(aq) + \mathrm{SO_4}^{2-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Ag}^{+}]^2[\mathrm{SO_4}^{2-}]$; (d) $\mathrm{Pb(OH)_2}(s) \rightleftharpoons \mathrm{Pb}^{2+}(aq) + 2\mathrm{OH}^{-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Pb}^{2+}][\mathrm{OH}^{-}]^2$

56. (a)1.77 × 10^{-7}; (b) 1.6 × 10^{-6}; (c) 2.2 × 10^{-9}; (d) 7.91 × 10^{-22}

57. (a) 2 × 10^{-2}*M*; (b) 1.5 × 10^{-3}*M*; (c) 2.27 × 10^{-9}*M*; (d) 2.2 × 10^{-10}*M*

58. (a) 6.4 × 10^{-9}*M* = [Ag^+], [Cl^-] = 0.025 *M* Check: $\dfrac{6.4 \times 10^{-9}\ M}{0.025\ M} \times 100\% = 2.6 \times 10^{-5}$,an insignificant change; (b) 2.2 × 10^{-5}*M* = [Ca^{2+}], [F^-] = 0.0013 *M* Check: $\dfrac{2.26 \times 10^{-5}\ M}{0.00133\ M} \times 100\% = 1.70\%$. This value is less than 5% and can be ignored. (c) 0.2238 *M* = $[\mathrm{SO_4}^{2-}]$; [Ag^+] = 7.4 × 10^{-3}*M* Check: $\dfrac{3.7 \times 10^{-3}}{0.2238} \times 100\% = 1.64 \times 10^{-2}\%$; the condition is satisfied. (d) [OH^-] = 2.8 × 10^{-3}*M*; 5.7 × 10^{-12}*M* = [Zn^{2+}] Check:

$\frac{5.7 \times 10^{-12}}{2.8 \times 10^{-3}} \times 100\% = 2.0 \times 10^{-7}\%$; *x* is less than 5% of [OH^-] and is, therefore, negligible.

59. (a) [Cl^-] = 7.6×10^{-3} *M* Check: $\frac{7.6 \times 10^{-3}}{0.025} \times 100\% = 30\%$ This value is too large to drop *x*. Therefore solve by using the quadratic equation: [Ti^+] = 3.1×10^{-2} *M* [Cl^-] = 6.1×10^{-3}
(b) [Ba^{2+}] = 7.7×10^{-4} *M* Check: $\frac{7.7 \times 10^{-4}}{0.0313} \times 100\% = 2.4\%$ Therefore, the condition is satisfied. [Ba^{2+}] = 7.7×10^{-4} *M* [F^-] = 0.0321 *M*; (c) $Mg(NO_3)_2$ = 0.02444 *M* $[C_2O_4{}^{2-}] = 2.9 \times 10^{-5}$ Check: $\frac{2.9 \times 10^{-5}}{0.02444} \times 100\% = 0.12\%$ The condition is satisfied; the above value is less than 5%. $[C_2O_4{}^{2-}] = 2.9 \times 10^{-5}\ M$ [Mg^{2+}] = 0.0244 *M* (d) [OH^-] = 0.0501 *M* [Ca^{2+}] = 3.15×10^{-3} Check: $\frac{3.15 \times 10^{-3}}{0.050} \times 100\% = 6.28\%$ This value is greater than 5%, so a more exact method, such as successive approximations, must be used. [Ca^{2+}] = 2.8×10^{-3} *M* [OH^-] = 0.053×10^{-2} *M*
60. $CaSO_4{\cdot}2H_2O$ is the most soluble Ca salt in mol/L, and it is also the most soluble Ca salt in g/L.
61. 4.8×10^{-3} *M* = $[SO_4{}^{2-}]$ = [Ca^{2+}]; Since this concentration is higher than 2.60×10^{-3} *M*, "gyp" water does not meet the standards.
62. Mass ($CaSO_4{\cdot}2H_2O$) = 0.72 g/L
63. (a) [Ag^+] = [I^-] = 1.3×10^{-5} *M*; (b) [Ag^+] = 2.88×10^{-2} *M*, $[SO_4{}^{2-}]$ = 1.44×10^{-2} *M*; (c) [Mn^{2+}] = 3.7×10^{-5} *M*, [OH^-] = 7.4×10^{-5} *M*; (d) [Sr^{2+}] = 4.3×10^{-2} *M*, [OH^-] = 8.6×10^{-2} *M*; (e) [Mg^{2+}] = 1.3×10^{-4} *M*, [OH^-] = 2.6×10^{-4} *M*.
64. (a) 2.0×10^{-4}; (b) 5.1×10^{-17}; (c) 1.35×10^{-4}; (d) 1.18×10^{-5}; (e) 1.08×10^{-10}
65. (a) $CaCO_3$ does precipitate. (b) The compound does not precipitate. (c) The compound does not precipitate. (d) The compound precipitates.
66. 3.03×10^{-7} *M*
67. 9.2×10^{-13} *M*
68. [Ag^+] = 1.8×10^{-3} *M*
69. 6.3×10^{-4}
70. (a) 2.25 L; (b) 7.2×10^{-7} g
71. 100% of it is dissolved
72. (a) $Hg_2{}^{2+}$ and Cu^{2+}: Add $SO_4{}^{2-}$. (b) $SO_4{}^{2-}$ and Cl^-: Add Ba^{2+}. (c) Hg^{2+} and Co^{2+}: Add S^{2-}. (d) Zn^{2+} and Sr^{2+}: Add OH^- until [OH^-] = 0.050 *M*. (e) Ba^{2+} and Mg^{2+}: Add $SO_4{}^{2-}$. (f) $CO_3{}^{2-}$ and OH^-: Add Ba^{2+}.
73. AgI will precipitate first.
74. 1.5×10^{-12} *M*
75. 3.99 kg
76. (a) 3.1×10^{-11}; (b) [Cu^{2+}] = 2.6×10^{-3}; $[IO_3{}^-]$ = 5.3×10^{-3}
77. 1.8×10^{-5} g $Pb(OH)_2$

78. $\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}} + \mathrm{2OH^-} \qquad K_{\mathrm{sp}} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2$
1.23×10^{-3} g $Mg(OH)_2$

79. $MnCO_3$ will form first, since it has the smallest K_{sp} value it is the least soluble. $MnCO_3$ will be the last to precipitate, it has the largest K_{sp} value.

80. The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

81. $[\mathrm{H_2O}] > [\mathrm{CH_3CO_2H}] > [\mathrm{H_3O^+}] \approx [\mathrm{CH_3CO_2}^-] > [\mathrm{OH^-}]$

82. The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

83. $\underset{\text{BB}}{\mathrm{Mg(OH)_2}(s)} + \underset{\text{BA}}{\mathrm{2HCl}(aq)} \longrightarrow \underset{\text{CB}}{\mathrm{Mg^{2+}}(aq)} + \underset{\text{CA}}{\mathrm{2Cl^-}(aq)} + \mathrm{2H_2O}(l)$ holy

84. $K_{\mathrm{a}} = 2.3 \times 10^{-11}$

85. The stronger base or stronger acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $\mathrm{CH_3NH_3}^+$.

86. triethylamine.

87. (a) $\mathrm{HSO_4}^-$; higher electronegativity of the central ion. (b) H_2O; NH_3 is a base and water is neutral, or decide on the basis of K_a values. (c) HI; PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI. (d) PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e) HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

88. (a) $\mathrm{NaHSeO_3} < \mathrm{NaHSO_3} < \mathrm{NaHSO_4}$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b) $\mathrm{ClO_2}^- < \mathrm{BrO_2}^- < \mathrm{IO_2}^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c) $\mathrm{HOI} < \mathrm{HOBr} < \mathrm{HOCl}$; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d) $\mathrm{HOCl} < \mathrm{HOClO} < \mathrm{HOClO_2} < \mathrm{HOClO_3}$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e) $\mathrm{HTe^-} < \mathrm{HS^-} \ll \mathrm{PH_2}^- < \mathrm{NH_2}^-$; $\mathrm{PH_2}^-$ and $\mathrm{NH_2}^-$ are anions of weak bases, so they act as strong bases toward H^+. HTe^- and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f) $\mathrm{BrO_4}^- < \mathrm{BrO_3}^- < \mathrm{BrO_2}^- < \mathrm{BrO^-}$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

89. $[\mathrm{H_2O}] > [\mathrm{C_6H_4OH(CO_2H)}] > [\mathrm{H^+}]_0 > [\mathrm{C_6H_4OH(CO_2)^-}] \gg [\mathrm{C_6H_4O(CO_2H)^-}] > [\mathrm{OH^-}]$

90. Strong electrolytes are 100% ionized, and, as long as the component ions are neither weak acids nor weak bases, the ionic species present result from the dissociation of the strong electrolyte. Equilibrium calculations are necessary when one (or more) of the ions is a weak acid or a weak base.

91. 1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

92. (b) The addition of HCl
93. (a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of $NO_2{}^-$ ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of $NO_2{}^-$ ions and decreasing the concentration of OH^- ions. (c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of $NO_2{}^-$ ions and decreasing the concentrations of HNO_2. (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding KNO_2 adds $NO_2{}^-$ ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.
94. This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.
95. (a) $K_b = 1.8 \times 10^{-5}$; (b) $K_a = 4.5 \times 10^{-4}$; (c) $K_b = 7.4 \times 10^{-5}$; (d) $K_a = 5.6 \times 10^{-10}$
96. $K_a = 1.2 \times 10^{-2}$
97. (a) $K_b = 4.3 \times 10^{-12}$; (b) $K_a = 1.6 \times 10^{-8}$; (c) $K_b = 5.9 \times 10^{-7}$; (d) $K_b = 4.2 \times 10^{-3}$; (e) $K_b = 2.3 \times 10^{-3}$; (f) $K_b = 6.3 \times 10^{-13}$
98. (a) is the correct statement.
99. $[H_3O^+] = 7.5 \times 10^{-3}\,M$ $[HNO_2] = 0.127$ $[OH^-] = 1.3 \times 10^{-12}\,M$ $[BrO^-] = 4.5 \times 10^{-8}\,M$ $[HBrO] = 0.120\,M$
100. $[OH^-] = [NO_4{}^+] = 0.0014\,M$ $[NH_3] = 0.144\,M$ $[H_3O^+] = 6.9 \times 10^{-12}\,M$ $[C_6H_5NH_3{}^+] = 3.9 \times 10^{-8}\,M$ $[C_6H_5NH_2] = 0.100\,M$
101. (a) $\frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$ Solving for x gives $1.63 \times 10^{-5}\,M$. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[H_3O^+] = [ClO] = 5.8 \times 10^{-5}\,M$ $[HClO] = 0.00092\,M$ $[OH^-] = 6.1 \times 10^{-10}\,M$; (b) $\frac{[C_6H_5NH_3{}^+][OH^-]}{[C_6H_5NH_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$ Solving for x gives $5.81 \times 10^{-6}\,M$. This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[CH_3CO_2{}^-] = [OH^-] = 5.8 \times 10^{-6}\,M$ $[C_6H_5NH_2] = 0.00784$ $[H_3O^+] = 1.7\times 10^{-9}\,M$;(c) $\frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$ Solving for x gives $6.30 \times 10^{-6}\,M$. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[H_3O^+] = [CN^-] = 6.3 \times 10^{-6}\,M$ $[HCN] = 0.0810\,M$ $[OH^-] = 1.6 \times 10^{-9}\,M$;(d) $\frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$ Solving for x gives $2.63 \times 10^{-3}\,M$. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[(CH_3)_3NH^+] = [OH^-] = 2.6 \times 10^{-3}\,M$ $[(CH_3)_3N] = 0.11\,M$

$[H_3O^+] = 3.8 \times 10^{-12} M$;(e) $\frac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6{}^{2+}]} = \frac{(x)(x)}{(0.120\ -\ x)} \approx \frac{(x)(x)}{0.120} = 1.6\ \times\ 10^{-7}$
Solving for x gives $1.39 \times 10^{-4} M$. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4} M$ $[Fe(H_2O)_6{}^{2+}] = 0.120\ M$ $[OH^-] = 7.2 \times 10^{-11} M$

102. pH = 2.41

103. $[C_{10}H_{14}N_2] = 0.049\ M$ $[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4} M$ $[C_{10}H_{14}N_2H_2{}^{2+}] = 1.4 \times 10^{-11} M$ $[OH^-] = 1.9 \times 10^{-4} M$ $[H_3O^+] = 5.3 \times 10^{-11} M$

104. $K_a = 1.2\ \times\ 10^{-2}$

105. $K_b = 1.77\ \times\ 10^{-5}$

106. 0.014 M

107. $7.2 \times 10^{-15} M$

108. $4.4 \times 10^{-22} M$

109. $6.2 \times 10^{-6} M = [Hg^{2+}]$; $1.2 \times 10^{-5} M = [Cl^-]$; The substance is a weak electrolyte because very little of the initial 0.015 M $HgCl_2$ dissolved.

110. $[OH^-] = 4.5 \times 10^{-5}$; $[Al^{3+}] = 2.2 \times 10^{-20}$ (molar solubility)

111. $[SO_4{}^{2-}] = 0.049\ M$ $[Ba^{2+}] = 4.7 \times 10^{-7}$ (molar solubility)

112. $[OH^-] = 7.6 \times 10^{-3} M$ $[Pb^{2+}] = 2.1 \times 10^{-11}$ (molar solubility)

113. 7.66

114. $[CO_3{}^{2-}] = 0.116\ M$ $[Cd^{2+}] = 4.5 \times 10^{-11} M$

115. $3.1 \times 10^{-3} M$

116. 0.0102 L (10.2 mL)

117. 5.4×10^{-3} g

118. (a) $K_{sp} = [Mg^{2+}][F^-]^2 = (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 = 7.09 \times 10^{-9}$; (b) $7.09 \times 10^{-7} M$ (c) Determine the concentration of Mg^{2+} and F^- that will be present in the final volume. Compare the value of the ion product $[Mg^{2+}][F^-]^2$ with K_{sp}. If this value is larger than K_{sp}, precipitation will occur. $0.1000\ L \times 3.00 \times 10^{-3} M\ Mg(NO_3)_2 = 0.3000\ L \times M\ Mg(NO_3)_2 M\ Mg(NO_3)_2 = 1.00 \times 10^{-3} M$ $0.2000\ L \times 2.00 \times 10^{-3} M\ NaF = 0.3000\ L \times M\ NaF\ M\ NaF = 1.33 \times 10^{-3} M$ ion product $= (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.77 \times 10^{-9}$ This value is smaller than K_{sp}, so no precipitation will occur. (d) MgF_2 is less soluble at 27 °C than at 18 °C. Because added heat acts like an added reagent, when it appears on the product side, the Le Châtelier's principle states that the equilibrium will shift to the reactants' side to counter the stress. Consequently, less reagent will dissolve. This situation is found in our case. Therefore, the reaction is exothermic.

119. BaF_2, $Ca_3(PO_4)_2$, ZnS; each is a salt of a weak acid, and the $[H_3O^+]$ from perchloric acid reduces the equilibrium concentration of the anion, thereby increasing the concentration of the cations

120. Effect on amount of solid $CaHPO_4$, $[Ca^{2+}]$, $[OH^-]$: (a) increase, increase, decrease; (b) decrease, increase, decrease; (c) no effect, no effect, no effect; (d) decrease, increase, decrease; (e) increase, no effect, no effect

121. 9.2 g

CHAPTER 18: OXIDATION-REDUCTION

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The defining traits of redox chemistry

- Identifying the oxidant and reductant of a redox reaction
- Balancing chemical equations for redox reactions using the half-reaction method
- The function of a galvanic cell and its components
- The definitions of electrodes and cell potentials
- The electrochemistry associated with several common batteries
- Corrosion
- The process of electrolysis

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Ionic and Covalent Compounds
- Chemical Reactions
- Chemical Stoichiometry

Figure 18a Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker, CC BY 2.0)

In this chapter we will be introducing the chemistry of reduction-oxidation (redox) reactions. This important reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred indirectly via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of electrochemistry has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (Figure 18.a). In this chapter, the essential concepts of electrochemistry will be addressed.

Attribution & References

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18.1 REDOX REACTIONS AND OXIDATION NUMBERS

Learning Objectives

By the end of this section, you will be able to:

- Identify the oxidation number for each element in a redox reaction
- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as **oxidation-reduction (redox) reactions**. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$2Na(s) \rightarrow 2Na^+(s) + 2e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\text{oxidation} = \text{loss of electrons}$$
$$\text{reduction} = \text{gain of electrons}$$

In this reaction, then, sodium is **oxidized** and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium.

$$\text{reducing agent} = \text{species that is oxidized}$$
$$\text{oxidizing agent} = \text{species that is reduced}$$

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called **oxidation number** has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess if the compound were ionic. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

Assigning Oxidation Numbers

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
    - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
    - Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, O_2^{2-}), very rarely −1/2 (so-called superoxides, O_2^{-}), positive values when combined with F (values vary)
    - Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)

4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example 18.1a

Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. H_2S
b. SO_3^{2-}
c. Na_2SO_4

Solution

a. According to guideline 3, the oxidation number for H is +1.
   Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:
   charge on $H_2S = 0 = (2 \times +1) + (1 \times \boldsymbol{x})$
   $\boldsymbol{x} = 0 - (2 \times +1) = -2$
b. Guideline 3 suggests the oxidation number for oxygen is −2.
   Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:
   charge on $SO_3^{2-} = -2 = (3 \times -2) + (1 \times \boldsymbol{x})$
   $\boldsymbol{x} = -2 - (3 \times -2) = +4$
c. For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.
   According to guideline 2, the oxidation number for sodium is +1.
   Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:
   charge on $SO_4^{2-} = -2 = (4 \times -2) + (1 \times \boldsymbol{x})$

$x = -2 - (4 \times -2) = +6$

Exercise 18.1a

Assign oxidation states to the elements whose atoms are underlined (the underlined elements are a. N, b. A, c. N, d. P) in each of the following compounds or ions:

a. $K\underline{N}O_3$
b. $\underline{Al}H_3$
c. $\underline{N}H_4^+$
d. $H_2\underline{P}O_4^-$

Check Your Answers[1]

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist as seen in Example 18.1b). Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\text{oxidation} = \text{increase in oxidation number}$$
$$\text{reduction} = \text{decrease in oxidation number}$$

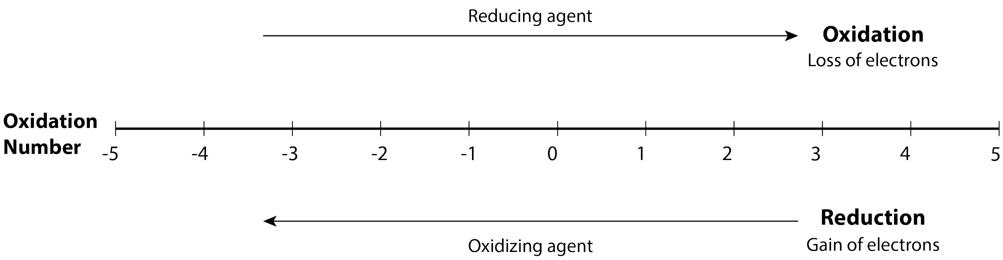

Figure 18.1a Oxidation is a loss of electrons. Reduction is a gain of electrons (credit: graphic by Revathi Mahadevan, CC BY 4.0).

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Several subclasses of redox reactions are recognized, including combustion reactions in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10Al(s) + 6NH_4ClO_4(s) \rightarrow 4Al_2O_3(s) + 2AlCl_3(s) + 12H_2O(g) + 3N_2(g)$$

The test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System is being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

Watch NASA Tests Model of Powerful New Rocket (0:30 min)

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 18.1b).

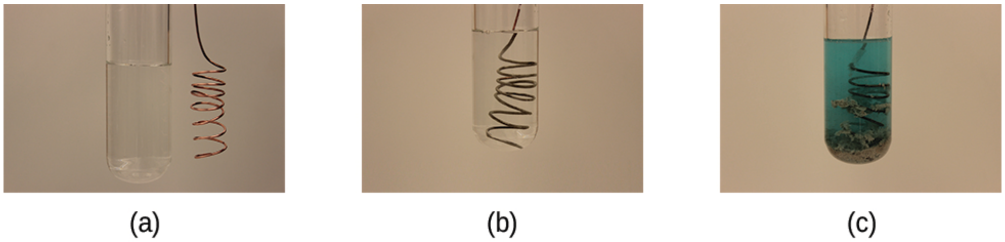

Figure 18.1b (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of grey-coloured silver metal on the wire and development of a blue colour in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

Example 18.1b

Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$
b. $2Ga(l) + 3Br_2(l) \rightarrow 2GaBr_3(s)$
c. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
d. $BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)$
e. $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in $Ga(l)$ to +3 in $GaBr_3(s)$. The reducing agent is $Ga(l)$. Bromine is reduced, its oxidation number decreasing from 0 in $Br_2(l)$ to −1 in $GaBr_3(s)$. The oxidizing agent is $Br_2(l)$.
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in $H_2O_2(aq)$ to 0 in $O_2(g)$. Oxygen is also reduced, its oxidation number decreasing from −1 in $H_2O_2(aq)$ to −2 in $H_2O(l)$. For disproportionation reactions, the same substance functions as an oxidant and a reductant.

d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in $C_2H_4(g)$ to +4 in $CO_2(g)$. The reducing agent (fuel) is $C_2H_4(g)$. Oxygen is reduced, its oxidation number decreasing from 0 in $O_2(g)$ to −2 in $H_2O(l)$. The oxidizing agent is $O_2(g)$.

Exercise 18.1b

This equation describes the production of tin(II) chloride:

$Sn(s) + 2HCl(g) \rightarrow SnCl_2(s) + H_2(g)$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant

Check Your Answer[2]

Links to Interactive Learning Tools

Explore Oxidation States from the Physics Classroom.

Explore Oxidation-Reduction from the Physics Classroom.

Attribution & References

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Notes

1. (a) N, +5; (b) Al, +3; (c) N, −3; (d) P, +5
2. Yes, a single-replacement reaction. Sn(*s*)is the reductant, HCl(*g*) is the oxidant.

18.2 BALANCING REDOX REACTIONS

Learning Objectives

By the end of this section, you will be able to:

- Balance chemical equations for redox reactions using the half-reaction method

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

Balancing Redox Reactions

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding H_2O molecules.
4. Balance hydrogen atoms by adding H^+ ions.
5. Balance charge by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.

8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
    a. Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
    b. On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
    c. Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges are balanced.

Example 18.2a

Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

Solution

Step 1. *Write the two half-reactions*. Each half-reaction will contain one reactant and one product with one element in common.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

Step 2. *Balance all elements except oxygen and hydrogen*. The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$$Fe^{2+} \rightarrow Fe^{3+}$$

$$Cr_2O_7^{2-} \rightarrow \mathbf{2}Cr^{3+}$$

Step 3. *Balance oxygen atoms by adding* H_2O *molecules*. The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$$Fe^{2+} \rightarrow Fe^{3+}$$

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + \mathbf{7H_2O}$$

Step 4. *Balance hydrogen atoms by adding* H^+ *ions*. The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$$Fe^{2}+ \rightarrow Fe^{3}+$$

$$Cr_2O_7^{2-} + \mathbf{14H^+} \rightarrow 2Cr^{3+} + 7H_2O$$

Step 5. *Balance charge by adding electrons*. The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} ion). Adding one electron to the right side brings that side's total charge to (3+) + (1−) = 2+, and charge balance is achieved. The chromium half-reaction shows a total charge of (1 × 2−) + (14 × 1+) = 12+ on the left side (1 $Cr_2O_7^{2-}$ ion and 14 H^+ ions). The total charge on the right side is (2 × 3+) = 6 + (2 Cr^{3+} ions). Adding six electrons to the left side will bring that side's total charge to (12^+ + 6^-) = 6+, and charge balance is achieved.

$$Fe^{2+} \rightarrow Fe^{3+} + \mathbf{e^-}$$

$$Cr_2O_7^{2-} + 14H^+ + \mathbf{6e^-} \rightarrow 2Cr^{3+} + 7H_2O$$

Step 6. *Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction*. To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$$\mathbf{6}Fe^{2+} \rightarrow \mathbf{6}Fe^{3+} + \mathbf{6e^-}$$

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

Step 7. *Add the balanced half-reactions and cancel species that appear on both sides of the equation.*

$$6Fe^{2+} + Cr_2O_7^{2-} + \mathbf{6e^-} + 14H^+ \rightarrow 6Fe^{3+} + \mathbf{6e^-} + 2Cr^{3+} + 7H_2O$$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

A final check of atom and charge balance confirms the equation is balanced.

Component	Reactants	Products
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

Exercise 18.2a

In acidic solution, hydrogen peroxide reacts with Fe^{2+} to produce Fe^{3+} and H_2O. Write a balanced equation for this reaction.

Check Your Answer[1]

Example 18.2b

Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, MnO_4^-, and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion, CrO_4^{2-}. The reaction takes place in a basic solution.

Solution

Following the steps of the half-reaction method:

Step 1. Write *skeletal equations for the oxidation and reduction half-reactions.*

$$\text{oxidation: } Cr(OH)_3(s) \rightarrow CrO_4^{2-}(aq)$$
$$\text{reduction: } MnO_4^-(aq) \rightarrow MnO_2(s)$$

Step 2. Balance *each half-reaction for all elements except H and O.*

$$\text{oxidation: } \mathrm{Cr(OH)_3(s) \rightarrow CrO_4{}^{2-}(aq)}$$
$$\text{reduction: } \mathrm{MnO_4{}^{-}(aq) \rightarrow MnO_2(s)}$$

Step 3. *Balance each half-reaction for O by adding H_2O.*

$$\text{oxidation: } \mathbf{H_2O(l)} + \mathrm{Cr(OH)_3(s) \rightarrow CrO_4{}^{2-}(aq)}$$
$$\text{reduction: } \mathrm{MnO_4{}^{-}(aq) \rightarrow MnO_2(s)} + \mathbf{2H_2O(l)}$$

Step 4. *Balance each half-reaction for H by adding H^+.*

$$\text{oxidation: } \mathrm{H_2O(l) + Cr(OH)_3(s) \rightarrow CrO_4{}^{2-}(aq)} + \mathbf{5H^+(aq)}$$
$$\text{reduction: } \mathbf{4H^+(aq)} + \mathrm{MnO_4{}^{-}(aq) \rightarrow MnO_2(s) + 2H_2O(l)}$$

Step 5. *Balance each half-reaction for charge by adding electrons.*

$$\text{oxidation: } \mathrm{H_2O(l) + Cr(OH)_3(s) \rightarrow CrO_4{}^{2-}(aq) + 5H^+(aq)} + \mathbf{3e^-}$$
$$\text{reduction: } \mathbf{3e^-} + \mathrm{4H^+(aq) + MnO_4{}^{-}(aq) \rightarrow MnO_2(s) + 2H_2O(l)}$$

If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other. This step is not necessary since the number of electrons is already in balance.

Add the two half-reactions and simplify.

$$\cancel{\mathrm{H_2O(l)}} + \mathrm{Cr(OH)_3(s)} + \cancel{\mathrm{3e^-}} + \cancel{\mathrm{4H}}\mathrm{^+(aq) + MnO_4{}^{-}(aq) \rightarrow CrO_4{}^{2-}(aq)} + \cancel{5}\mathrm{H^+(aq)} + \cancel{\mathrm{3e^-}} + \mathrm{MnO_2(s)} + \cancel{2}\mathrm{H_2O(l)}$$
$$\mathrm{Cr(OH)_3(s) + MnO_4{}^{-}(aq) \rightarrow CrO_4{}^{2-}(aq) + H^+(aq) + MnO_2(s) + H_2O(l)}$$

If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

$$\mathbf{OH^-(aq)} + \mathrm{Cr(OH)_3(s) + MnO_4{}^{-}(aq) \rightarrow CrO_4{}^{2-}(aq) + H^+(aq)} + \mathbf{OH^-(aq)} + \mathrm{MnO_2(s) + H_2O(l)}$$
$$\mathrm{OH^-(aq) + Cr(OH)_3(s) + MnO_4{}^{-}(aq) \rightarrow CrO_4{}^{2-}(aq) + MnO_2(s)} + \mathbf{2H_2O(l)}$$

Exercise 18.2b

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, $BrO_3{}^-$. Write the balanced equation for this reaction occurring in a basic medium.

Check Your Answer[2]

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "7.2 Classifying Chemical Reactions" and "17.1 Review of Redox Chemistry" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*.

Notes

1. $H_2O_2(aq) + 2H^+(aq) + 2Fe^{2+} \rightarrow 2H_2O(l) + 2Fe^{3+}$
2. $H_2O(l) + 2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$

18.3 GALVANIC CELLS

Learning Objectives

By the end of this section, you will be able to:

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as **voltaic cells**, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure 18.3a). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue colour of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\begin{array}{lrl}
\text{oxidation:} & \text{Cu}(s) & \longrightarrow \text{Cu}^{2+}(aq) + 2\text{e}^- \\
\text{reduction:} & 2 \times [\text{Ag}^+(aq) + \text{e}^- & \longrightarrow \text{Ag}(s)] \quad \text{or} \quad 2\text{Ag}^+(aq) + 2\text{e}^- \longrightarrow \text{Ag}(s) \\
\hline
\text{overall:} & 2\text{Ag}^+(aq) + \text{Cu}(s) & \longrightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(aq)
\end{array}$$

The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

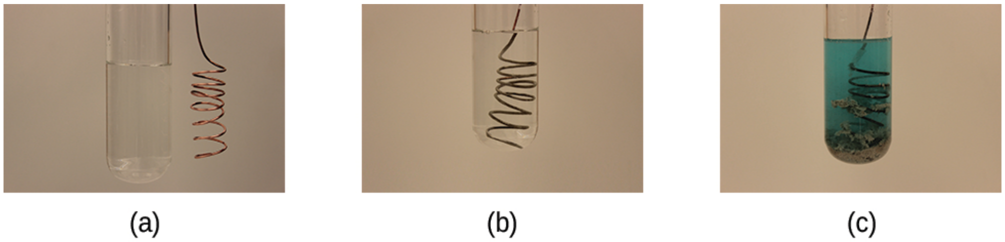

Figure 18.3a When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^{+} ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure 18.3b) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 M solution of copper(II) nitrate [$Cu(NO_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the **anode**. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the **cathode**. The half-cell on the right side of the figure consists of the silver electrode in a 1 M solution of silver nitrate ($AgNO_3$). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations "replace" the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the **cell potential.** The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

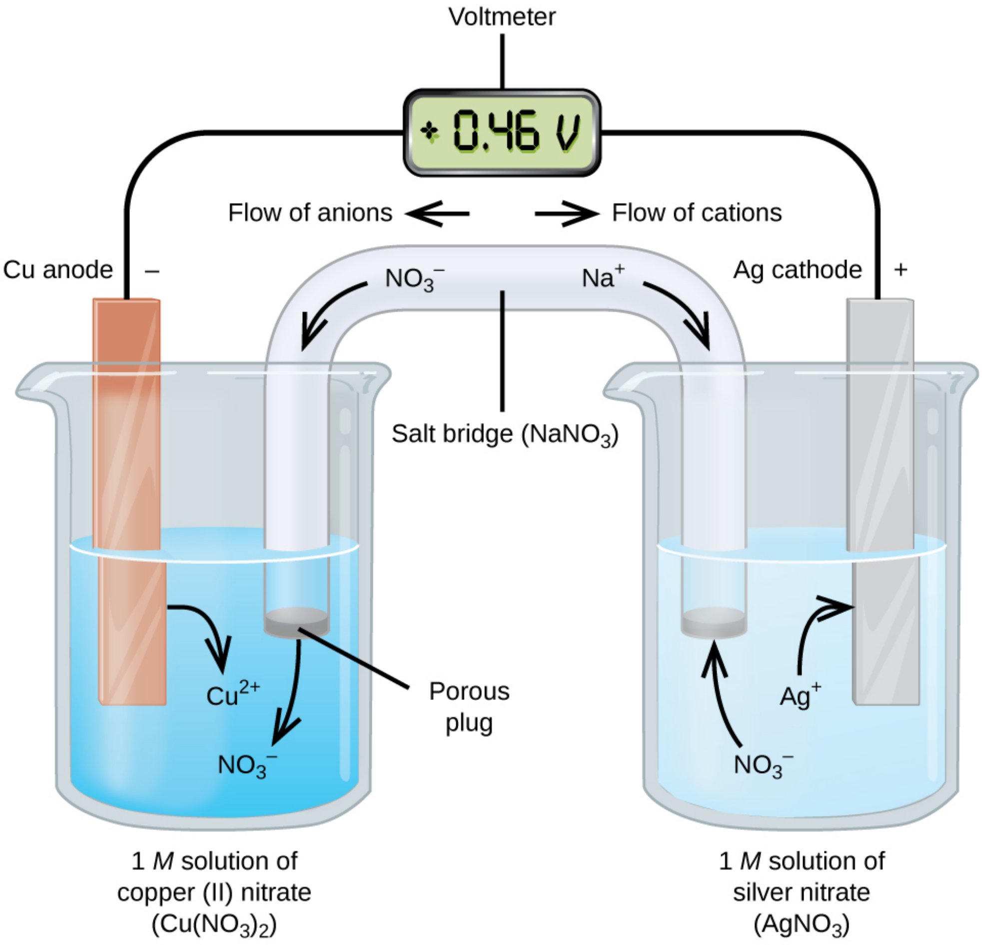

Figure 18.3b In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction and that the electrons are flowing from the left to the right. There is a lot going on in Figure 18.3b, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).

- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The **cell notation** (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, **|**, denotes a phase boundary and a double line, ‖, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in Figure 18.3b is then

$$\mathrm{Cu}(s)|\mathrm{Cu}^{2+}(aq,\,1\ M)||\mathrm{Ag}^{+}(aq,\,1\ M)|\mathrm{Ag}(s)$$

Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in Figure 18.3c. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\begin{array}{lrl}
\text{oxidation:} & \mathrm{Mg}(s) & \longrightarrow \mathrm{Mg}^{2+}(aq)\ +\ 2\mathrm{e}^{-} \\
\text{reduction:} & 2\mathrm{H}^{+}(aq)\ +\ 2\mathrm{e}^{-} & \longrightarrow \mathrm{H}_2(g) \\
\hline
\text{overall:} & \mathrm{Mg}(s)\ +\ 2\mathrm{H}^{+}(aq) & \longrightarrow \mathrm{Mg}^{2+}(aq)\ +\ \mathrm{H}_2(g)
\end{array}$$

The cell used an inert platinum wire for the cathode, so the cell notation is

$$\mathrm{Mg}(s)|\mathrm{Mg}^{2+}(aq)||\mathrm{H}^{+}(aq)|\mathrm{H}_2(g)|\mathrm{Pt}(s)$$

The magnesium electrode is an **active electrode** because it participates in the oxidation-reduction reaction. **Inert electrodes**, like the platinum electrode in Figure 18.3c, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

Example 18.3a

Using Cell Notation

Consider a galvanic cell consisting of

$$2\text{Cr}(s) \ + \ 3\text{Cu}^{2+}(aq) \longrightarrow 2\text{Cr}^{3+}(aq) \ + \ 3\text{Cu}(s)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+}, and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives

$$\begin{array}{lrl}
\textbf{oxidation:} & 2\text{Cr}(s) & \longrightarrow 2\text{Cr}^{3+}(aq) \ + \ 6\text{e}^- \\
\textbf{reduction:} & 3\text{Cu}^{2+}(aq) \ + \ 6\text{e}^- & \longrightarrow 3\text{Cu}(s) \\
\hline
\textbf{overall:} & 2\text{Cr}(s) \ + \ 3\text{Cu}^{2+}(aq) & \longrightarrow 2\text{Cr}^{3+}(aq) \ + \ 3\text{Cu}(s)
\end{array}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$\text{Cr}(s)|\text{Cr}^{3+}(aq)||\text{Cu}^{2+}(aq)|\text{Cu}(s)$. Oxidation occurs at the anode and reduction at the cathode.

Example 18.3b

Using Cell Notation

Consider a galvanic cell consisting of

$$5\text{Fe}^{2+}(aq) \ + \ \text{MnO}_4{}^-(aq) \ + \ 8\text{H}^+(aq) \longrightarrow 5\text{Fe}^{3+}(aq) \ + \ \text{Mn}^{2+}(aq) \ + \ 4\text{H}_2\text{O}(l)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+}, and MnO_4^- is reduced as it gains five electrons to form Mn^{2+}. Balancing the charge gives

$$\begin{array}{lrl}
\text{oxidation:} & 5 \times [\mathrm{Fe}^{2+}(aq) & \longrightarrow \mathrm{Fe}^{3+}(aq) + \mathrm{e}^-] \\
\text{reduction:} & \mathrm{MnO_4}^-(aq) + 8\mathrm{H}^+(aq) + 5\mathrm{e}^- & \longrightarrow \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l) \\
\hline
\text{overall:} & 5\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^-(aq) + 8\mathrm{H}^+(aq) & \longrightarrow 5\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l)
\end{array}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so: $\mathrm{Pt}(s)|\mathrm{Fe}^{2+}(aq),\ \mathrm{Fe}^{3+}(aq)||\mathrm{MnO_4}^-(aq),\ \mathrm{H}^+(aq),\ \mathrm{Mn}^{2+}(aq)|\mathrm{Pt}(s)$. Oxidation occurs at the anode and reduction at the cathode.

Exercise 18.3a

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Check Your Answer[1]

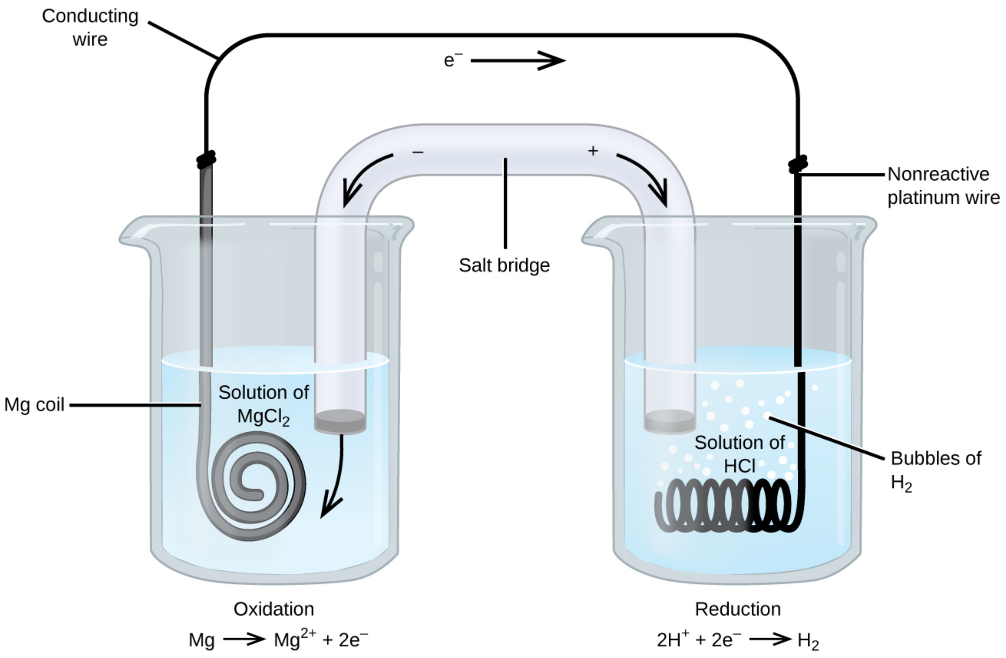

Figure 18.3c The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$, which is represented in cell notation as: $Mg(s) \mid Mg^{2+}(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$ (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Links to Interactive Learning Tools

Explore Galvanic Cells from the Physics Classroom.

Key Equations

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$

Attribution & References

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Notes

1. From the information given in the problem:

$$\begin{array}{lrl} \text{anode (oxidation):} & \text{Zn}(s) & \longrightarrow \text{Zn}^{2+}(aq) + 2\text{e}^- \\ \text{cathode (reduction):} & \text{Cu}^{2+}(aq) + 2\text{e}^- & \longrightarrow \text{Cu}(s) \\ \hline \text{overall:} & \text{Zn}(s) + \text{Cu}^{2+}(aq) & \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \end{array}$$

Using cell notation: $\text{Zn}(s)|\text{Zn}^{2+}(aq)||\text{Cu}^{2+}(aq)|\text{Cu}(s)$.

18.4 ELECTRODE AND CELL POTENTIALS

Learning Objectives

By the end of this section, you will be able to:

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential in 18.3 – Galvanic Cells results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in Figure 18.4a and is called the **standard hydrogen electrode (SHE)**. The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\text{H}^+(aq,\ 1\ M)\ +\ 2\text{e}^- \rightleftharpoons \text{H}_2(g,\ 1\ \text{atm}) \qquad E^\circ = 0\ \text{V}$$

$E°$ is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

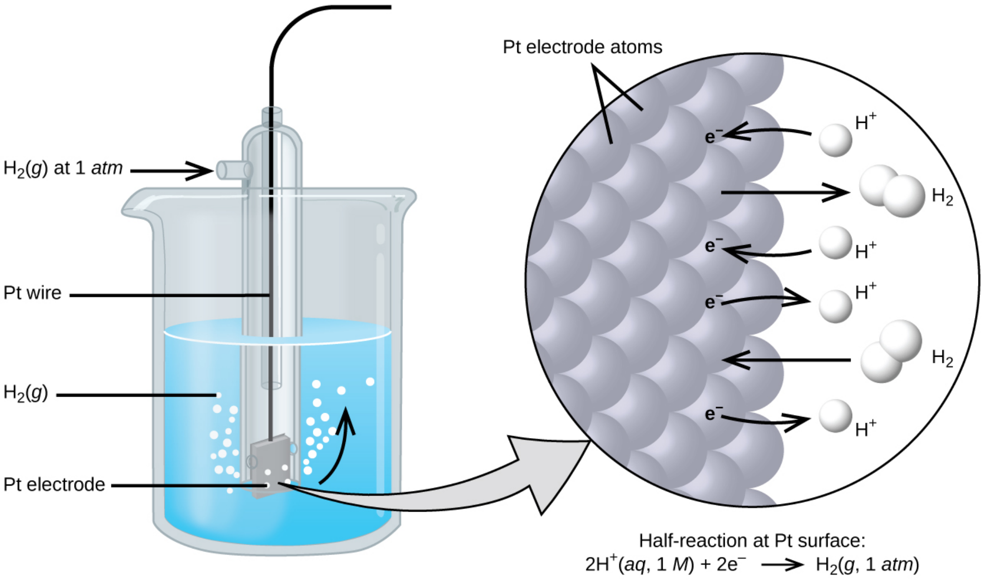

Figure 18.4a Hydrogen gas at 1 atm is bubbled through 1 *M* HCl solution. Platinum, which is inert to the action of the 1 *M* HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 18.4b). In cell notation, the reaction is

$$\text{Pt}(s)|\text{H}_2(g, 1\ \text{atm})|\text{H}^+(aq,\ 1\ M)||\text{Cu}^{2+}(aq,\ 1\ M)|\text{Cu}(s)$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{array}{lrl}
\text{Anode (oxidation):} & \text{H}_2(g) & \longrightarrow 2\text{H}^+(aq)\ +\ 2\text{e}^- \\
\text{Cathode (reduction):} & \text{Cu}^{2+}(aq)\ +\ 2\text{e}^- & \longrightarrow \text{Cu}(s) \\
\hline
\text{Overall:} & \text{Cu}^{2+}(aq)\ +\ \text{H}_2(g) & \longrightarrow 2\text{H}^+(aq)\ +\ \text{Cu}(s)
\end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}}\ -\ E^\circ_{\text{anode}}$$
$$+0.34\ \text{V} = E^\circ_{\text{Cu}^{2+}/\text{Cu}}\ -\ E^\circ_{\text{H}^+/\text{H}_2} = E^\circ_{\text{Cu}^{2+}/\text{Cu}}\ -\ 0 = E^\circ_{\text{Cu}^{2+}/\text{Cu}}$$

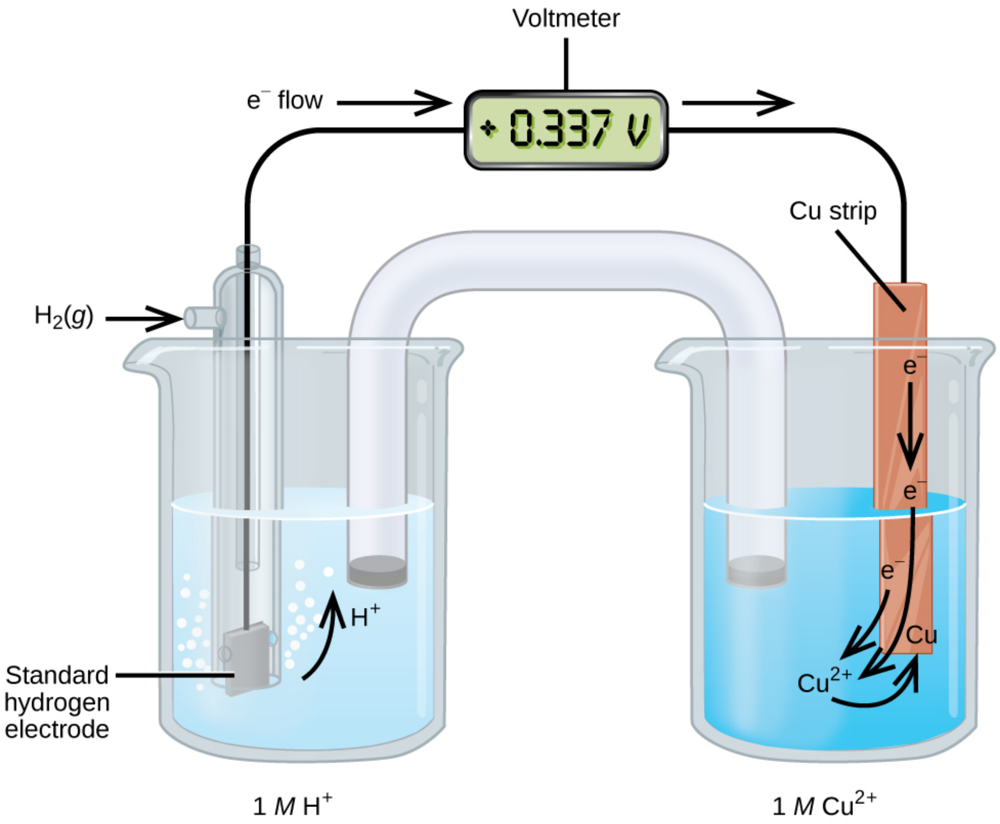

Figure 18.4b A galvanic cell can be used to determine the standard reduction potential of Cu^{2+} in *Chemistry (OpenStax)*, CC BY 4.0).

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure 18.4c, where

$$\text{Pt}(s)|\text{H}_2(\text{g, 1 atm})|\text{H}^+(\text{aq, 1 M})\|\text{Ag}^+(\text{aq, 1 M})|\text{Ag}(s)$$

Electrons flow from left to right, and the reactions are

$$\begin{array}{lrcl} \text{anode (oxidation):} & \text{H}_2(g) & \longrightarrow & 2\text{H}^+(aq) + 2\text{e}^- \\ \text{cathode (reduction):} & 2\text{Ag}^+(aq) + 2\text{e}^- & \longrightarrow & 2\text{Ag}(s) \\ \hline \text{overall:} & 2\text{Ag}^+(aq) + \text{H}_2(g) & \longrightarrow & 2\text{H}^+(aq) + 2\text{Ag}(s) \end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$
$$+0.80\text{ V} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{H}^+/\text{H}_2} = E^\circ_{\text{Ag}^+/\text{Ag}} - 0 = E^\circ_{\text{Ag}^+/\text{Ag}}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the **standard cell potential**, E°_{cell}, for any cell. For example, for the cell shown in Figure 18.3b in 18.3 – Galvanic Cells.

$$\text{Cu}(s)|\text{Cu}^{2+}(\text{aq, 1 M})\|\text{Ag}^{+}(\text{aq, 1 M})|\text{Ag}(s)$$

$$\begin{array}{lrl} \text{anode (oxidation):} & \text{Cu}(s) & \longrightarrow \text{Cu}^{2+}(aq) + 2\text{e}^- \\ \text{cathode (reduction):} & 2\text{Ag}^+(aq) + 2\text{e}^- & \longrightarrow 2\text{Ag}(s) \\ \hline \text{overall:} & \text{Cu}(s) + 2\text{Ag}^+(aq) & \longrightarrow \text{Cu}^{2+}(aq) + 2\text{Ag}(s) \end{array}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.80\text{ V} - 0.34\text{ V} = 0.46\text{ V}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table 2. A more complete list is provided in Appendix M.

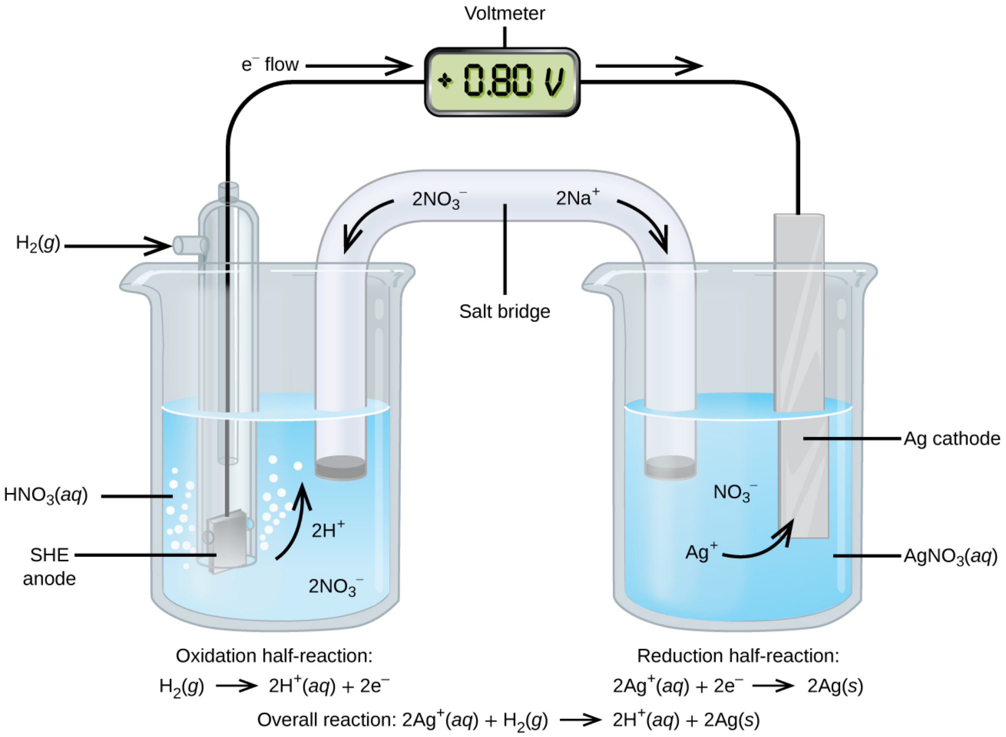

Figure 18.4c A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero in *Chemistry (OpenStax)*, CC BY 4.0).

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

Table 18.4a Selected Standard Reduction Potentials at 25 °C

Half-Reaction	***E*° (V)**
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.337
$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + 2e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.126
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.1262
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.185

Half-Reaction	***E*° (V)**
$Zn(OH)_2(s) + 2e^- \longrightarrow Zn(s) + 2OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.662
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.372
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.868
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.912
$K^+(aq) + e^- \longrightarrow K(s)$	−2.931
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.04

Example 18.4a

Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table 18.4a, the reactions involved in the galvanic cell, both written as reductions, are

$$\begin{aligned} \mathrm{Au^{3+}}(aq) \ + \ 3\mathrm{e^-} &\longrightarrow \mathrm{Au}(s) \qquad E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498 \text{ V} \\ \mathrm{Ni^{2+}}(aq) \ + \ 2\mathrm{e^-} &\longrightarrow \mathrm{Ni}(s) \qquad E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257 \text{ V} \end{aligned}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\begin{array}{llll} \text{Anode (oxidation):} & \mathrm{Ni}(s) & \longrightarrow \mathrm{Ni^{2+}}(aq) \ + \ 2\mathrm{e^-} & E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257 \text{ V} \\ \text{Cathode (reduction):} & \mathrm{Au^{3+}}(aq) \ + \ 3\mathrm{e^-} & \longrightarrow \mathrm{Au}(s) & E^\circ_{\text{cathode}} = E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498 \text{ V} \end{array}$$

The least common factor is six, so the overall reaction is

$$3\mathrm{Ni}(s) \ + \ 2\mathrm{Au^{3+}}(aq) \longrightarrow 3\mathrm{Ni^{2+}}(aq) \ + \ 2\mathrm{Au}(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 1.498 \text{ V} - (-0.257 \text{ V}) = 1.755 \text{ V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 18.4a

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Check Your Answer[1]

Key Equations

- $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$

Attribution & References

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Notes

1. $Mg(s) + 2Ag^{+}(aq) \longrightarrow Mg^{2+}(aq) + 2Ag(s) \qquad E^{\circ}_{\text{cell}} = 0.7996 \text{ V} - (-2.372 \text{ V}) = 3.172 \text{ V}$

18.5 BATTERIES AND FUEL CELLS

Learning Objectives

By the end of this section, you will be able to:

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A **battery** is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is "best" and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

Watch **Dry Cell – Definition, Working Principle, History, Parts of Dry Cell, Chemical reactions (4:48 min)**

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the **dry cell** (Figure 18.5a). The dry cell is a zinc-carbon battery. The zinc can serve as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) \ + \ 2\mathrm{e}^- \qquad E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.7618 \text{ V}$$

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately:

$$2\text{MnO}_2(s) + 2\text{NH}_4\text{Cl}(aq) + 2\text{e}^- \longrightarrow \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l) + 2\text{Cl}^-$$

The overall reaction for the zinc–carbon battery can be represented as:

$$2\text{MnO}_2(s) + 2\text{NH}_4\text{Cl}(aq) + \text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l) + 2\text{Cl}^-$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.

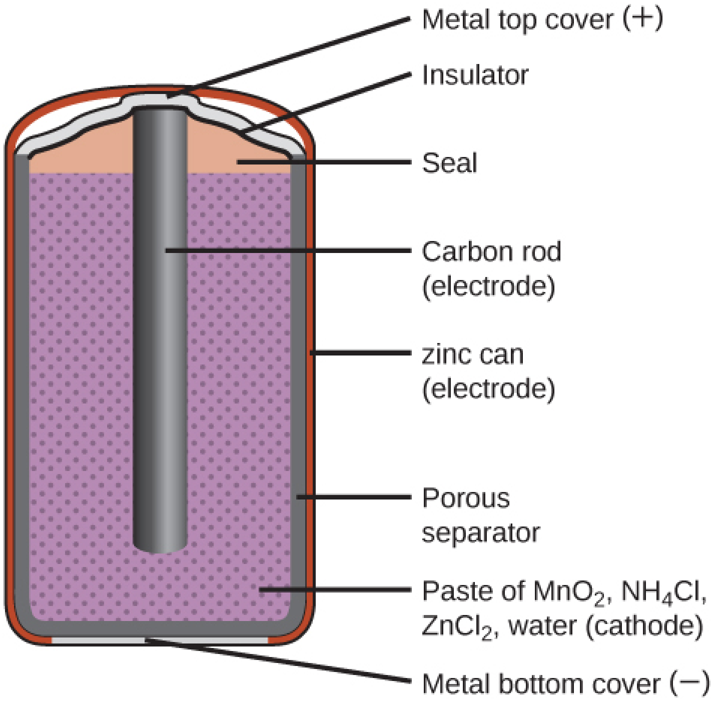

Figure 18.5a The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch Single-use cells & batteries (2:47 min)

Alkaline batteries (Figure 18.5b) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{array}{llll}
\text{anode:} & \mathrm{Zn}(s) + 2\mathrm{OH}^-(aq) & \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O}(l) + 2\mathrm{e}^- & E^\circ_\text{anode} = -1.28\ \mathrm{V} \\
\text{cathode:} & 2\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\mathrm{e}^- & \longrightarrow \mathrm{Mn_2O_3}(s) + 2\mathrm{OH}^-(aq) & E^\circ_\text{cathode} = +0.15\ \mathrm{V} \\
\hline
\text{overall:} & \mathrm{Zn}(s) + 2\mathrm{MnO_2}(s) & \longrightarrow \mathrm{ZnO}(s) + \mathrm{Mn_2O_3}(s) & E^\circ_\text{cell} = +1.43\ \mathrm{V}
\end{array}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

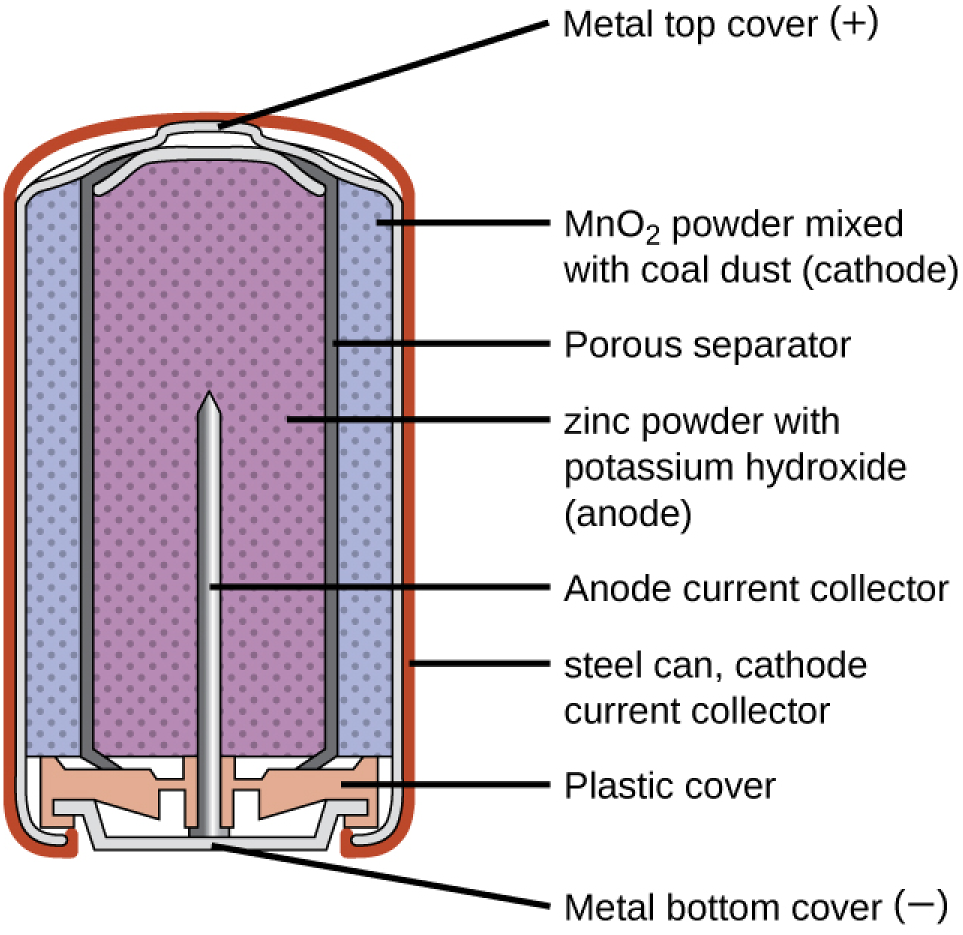

Figure 18.5b Alkaline batteries were designed as direct replacements for zinc-carbon (dry cell) batteries (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries (Figure 18.5c) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{array}{lrl} \text{anode:} & Cd(s) + 2OH^-(aq) & \longrightarrow Cd(OH)_2(s) + 2e^- \\ \text{cathode:} & NiO_2(s) + 2H_2O(l) + 2e^- & \longrightarrow Ni(OH)_2(s) + 2OH^-(aq) \\ \hline \text{overall:} & Cd(s) + NiO_2(s) + 2H_2O(l) & \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s) \end{array}$$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

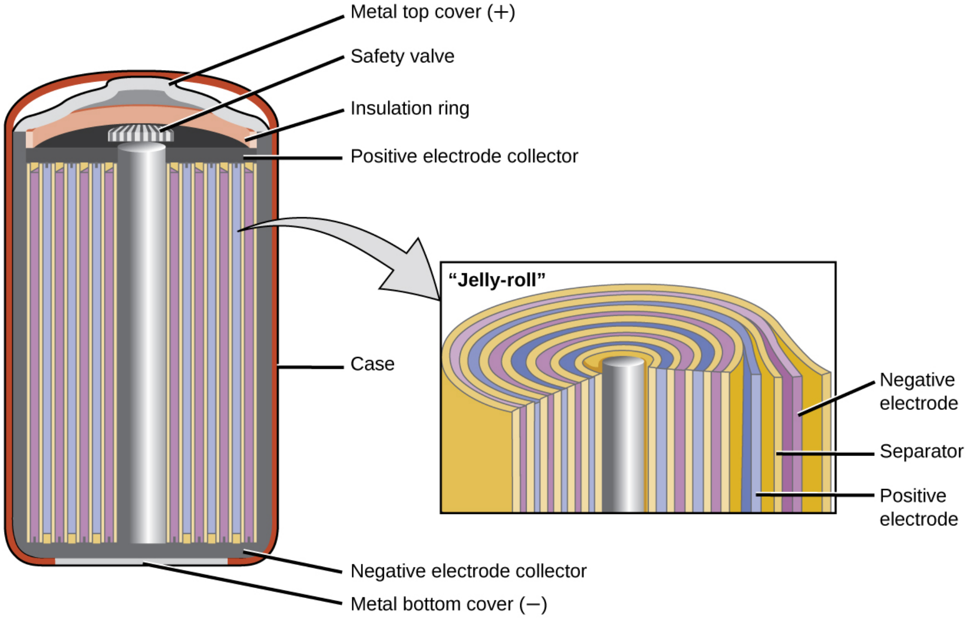

Figure 18.5c NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Lithium ion batteries (Figure 18.5d) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{lrl} \text{anode:} & LiCoO_2 & \leftrightharpoons Li_{x-1}CoO_2 + x\,Li^+ + x\,e^- \\ \text{cathode:} & x\,Li^+ + x\,e^- + x\,C_6 & \leftrightharpoons x\,LiC_6 \\ \hline \text{overall:} & LiCoO_2 + x\,C_6 & \leftrightharpoons Li_{x-1}CoO_2 + x\,LiC_6 \end{array}$$

With the coefficients representing moles, *x* is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount of current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

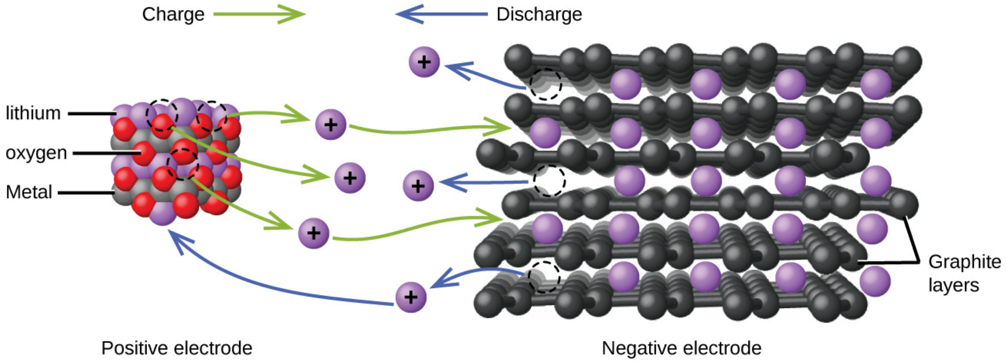

Figure 18.5d In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The **lead acid battery** (Figure 18.5e) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{array}{lrl}
\text{anode:} & \mathrm{Pb}(s) + \mathrm{HSO_4}^-(aq) & \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H}^+(aq) + 2\mathrm{e}^- \\
\text{cathode:} & \mathrm{PbO_2}(s) + \mathrm{HSO_4}^-(aq) + 3\mathrm{H}^+(aq) + 2\mathrm{e}^- & \longrightarrow \mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l) \\
\hline
\text{overall:} & \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\mathrm{H_2SO_4}(aq) & \longrightarrow 2\mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l)
\end{array}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

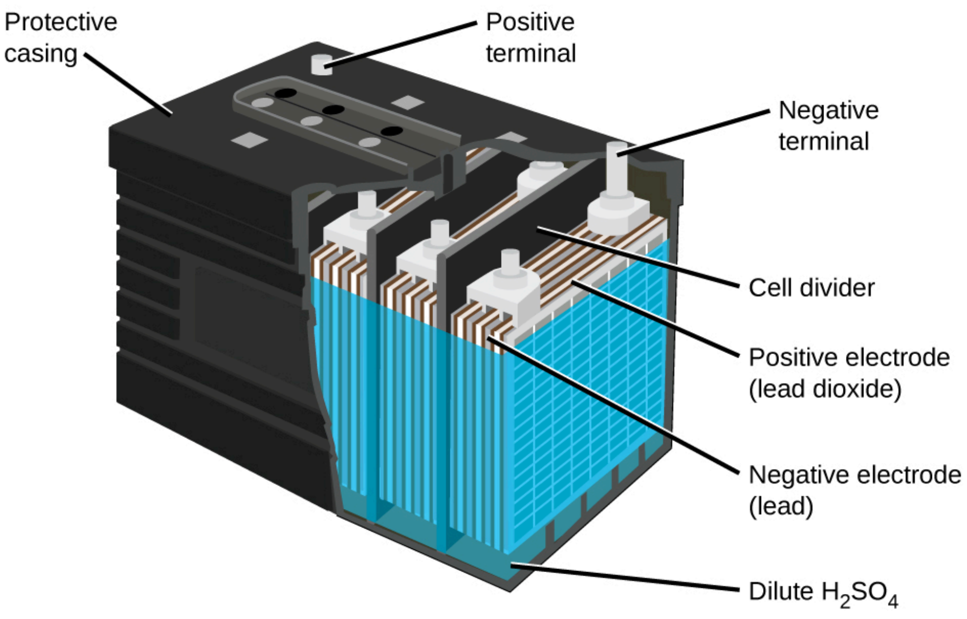

Figure 18.5e The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch How a lead-acid battery works (4:55 min)

Fuel Cells

A **fuel cell** is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure 18.5f).

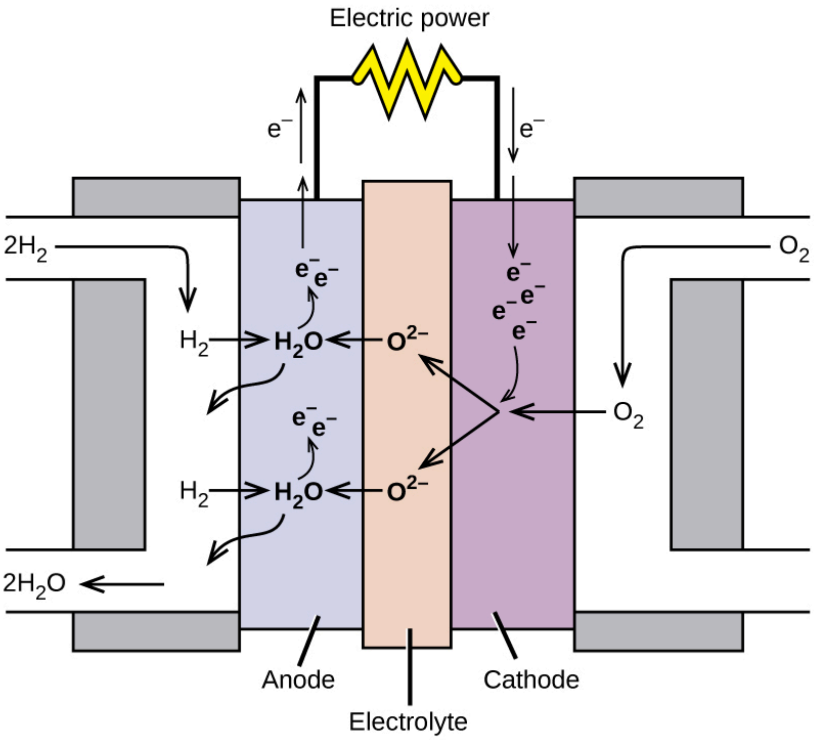

Figure 18.5f In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity (credit: *Chemistry (OpenStax)*, CC BY 4.0).

In a hydrogen fuel cell, the reactions are

$$\begin{array}{lrcl} \text{anode:} & 2H_2 + 2O^{2-} & \longrightarrow & 2H_2O + 4e^- \\ \text{cathode:} & O_2 + 4e^- & \longrightarrow & 2O^{2-} \\ \hline \text{overall:} & 2H_2 + O_2 & \longrightarrow & 2H_2O \end{array}$$

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Watch Hydrogen Fuel Cell (1:17 min)

Attribution & References

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18.6 CORROSION

Learning Objectives

By the end of this section, you will be able to:

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Statue of Liberty: Changing Colours

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green colour (Figure 18.6a). When this statue was first delivered from France, its appearance was not green. It was brown, the colour of its copper “skin.” So how did the Statue of Liberty change colours? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occurs in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

$$2\text{Cu}(s) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{Cu}_2\text{O}(s) \qquad \text{(red)}$$

$$\text{Cu}_2\text{O}(s) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow 2\text{CuO}(s) \qquad \text{(black)}$$

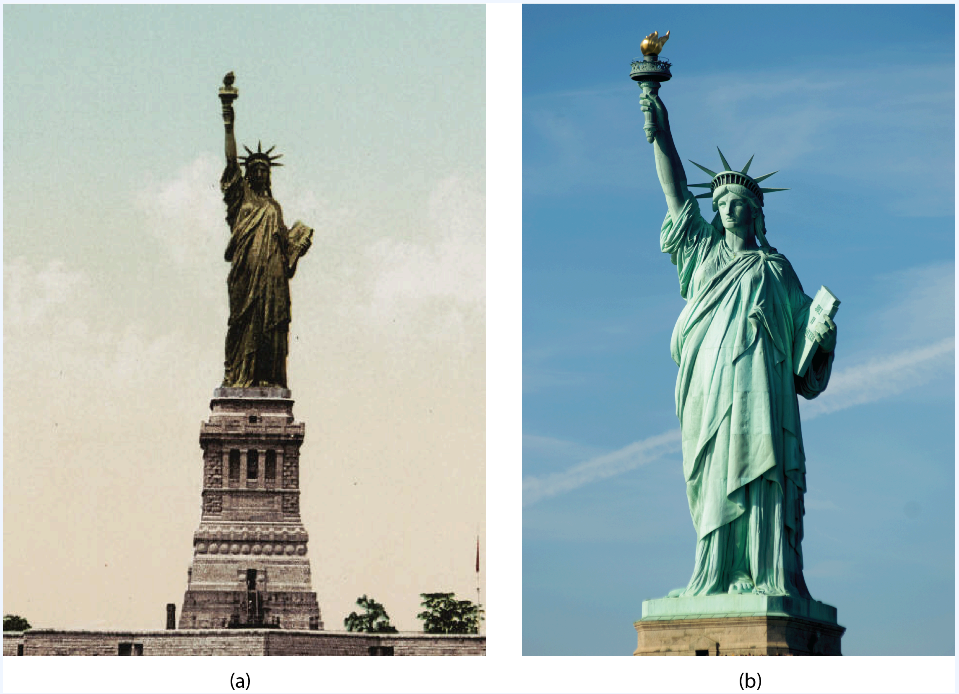
Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the CuO

$$2\mathrm{CuO}(s) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Cu_2CO_3(OH)_2}(s) \qquad \text{(green)}$$

$$3\mathrm{CuO}(s) + 2\mathrm{CO_2}(g) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Cu_2(CO_3)_2(OH)_2}(s) \qquad \text{(blue)}$$

$$4\mathrm{CuO}(s) + \mathrm{SO_3}(g) + 3\mathrm{H_2O}(l) \longrightarrow \mathrm{Cu_4SO_4(OH)_6}(s) \qquad \text{(green)}$$

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.



(a)

(b)

Figure 18.6a (a) The Statue of Liberty is covered with copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today. (credit a: work published by Detroit Photographic Company, PD; credit b: work by Dominique James, CC BY 2.0)

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following (Figure 18.6b). Once exposed to the atmosphere, iron rapidly oxidizes.

$$\text{anode: } \mathrm{Fe}(s) \longrightarrow \mathrm{Fe^{2+}}(aq) + 2\mathrm{e^-} \qquad E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\text{cathode: } \mathrm{O_2}(g) + 4\mathrm{H^+}(aq) + 4\mathrm{e^-} \longrightarrow 2\mathrm{H_2O}(l) \qquad E^\circ_{\mathrm{O_2/O^2}} = +1.23\ \mathrm{V}$$

$$\text{overall: } 2\mathrm{Fe}(s) + \mathrm{O_2}(g) + 4\mathrm{H^+}(aq) \longrightarrow 2\mathrm{Fe^{2+}}(aq) + 2\mathrm{H_2O}(l) \qquad E^\circ_{\mathrm{cell}} = +1.67\ \mathrm{V}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\text{Fe}^{2+}(aq) + \text{O}_2(g) + (4 + 2x)\,\text{H}_2\text{O}(l) \longrightarrow 2\text{Fe}_2\text{O}_3{\cdot}x\text{H}_2\text{O}(s) + 8\text{H}^+(aq)$$

The number of water molecules is variable, so it is represented by x. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

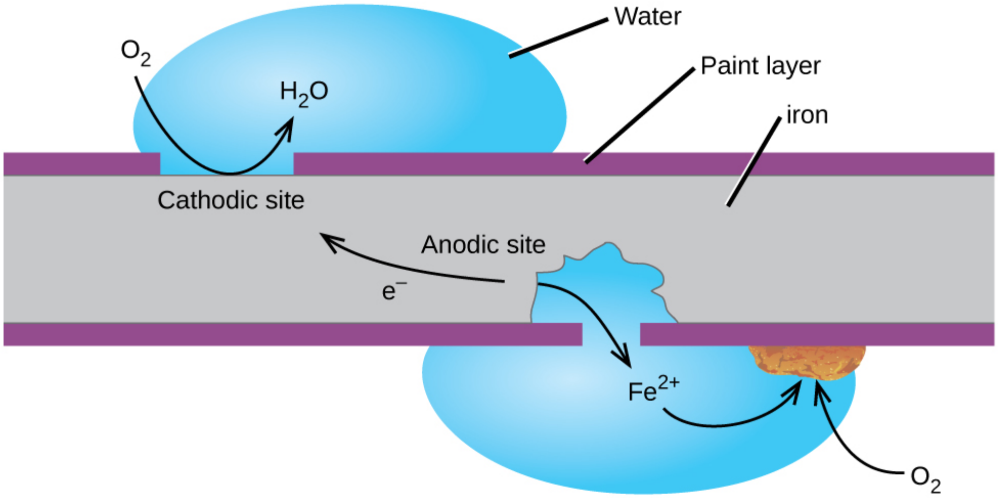


Figure 18.6b Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water (credit: *Chemistry (OpenStax)*, CC BY 4.0).

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or **galvanized iron** uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (Figure 18.6c). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

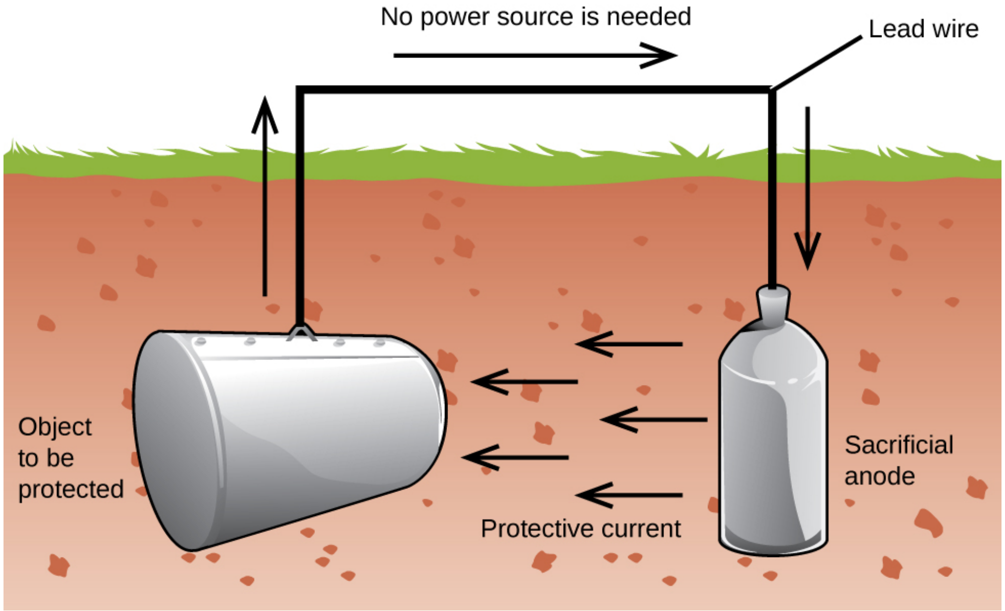


Figure 18.6c One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Attribution & References

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18.7 ELECTROLYSIS

Learning Objectives

By the end of this section, you will be able to:

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In **electrolytic cells**, electrical energy causes nonspontaneous reactions to occur in a process known as **electrolysis**. The charging electric car pictured in the Chapter 18 Introduction at the beginning of this chapter shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile.

The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure 18.7a. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\begin{array}{llll} \text{anode:} & 2\text{Cl}^-(l) & \longrightarrow \text{Cl}_2(g) + 2\text{e}^- & E^\circ_{\text{Cl}_2/\text{Cl}^-} = +1.3\text{ V} \\ \text{cathode:} & \text{Na}^+(l) + \text{e}^- & \longrightarrow \text{Na}(l) & E^\circ_{\text{Na}^+/\text{Na}} = -2.7\text{ V} \\ \hline \text{overall:} & 2\text{Na}^+(l) + 2\text{Cl}^-(l) & \longrightarrow 2\text{Na}(l) + \text{Cl}_2(g) & E^\circ_{\text{cell}} = -4.0\text{ V} \end{array}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

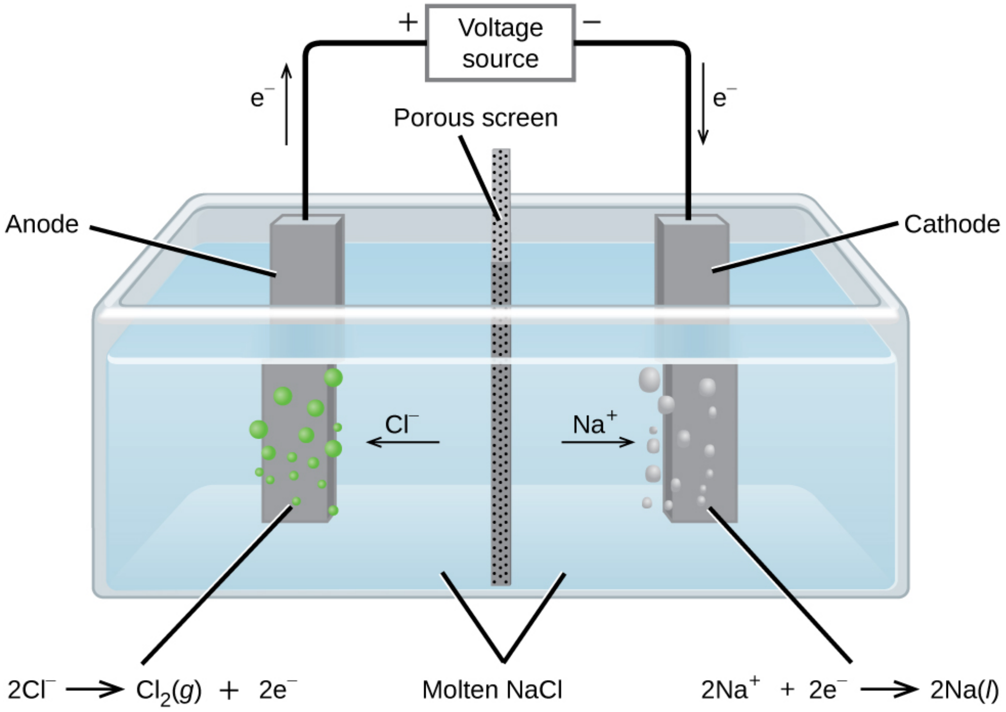

Figure 18.7a Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure 18.7b). The reactions are

$$\begin{array}{llll}
\text{anode:} & 2\mathrm{H_2O}(l) & \longrightarrow \mathrm{O_2}(g) + 4\mathrm{H^+}(aq) + 4\mathrm{e^-} & E^\circ_{\text{anode}} = +1.229\ \mathrm{V} \\
\text{cathode:} & 2\mathrm{H^+}(aq) + 2\mathrm{e^-} & \longrightarrow \mathrm{H_2}(g) & E^\circ_{\text{cathode}} = 0.000\ \mathrm{V} \\
\hline
\text{overall:} & 2\mathrm{H_2O}(l) & \longrightarrow 2\mathrm{H_2}(g) + \mathrm{O_2}(g) & E^\circ_{\text{cell}} = -1.229\ \mathrm{V}
\end{array}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

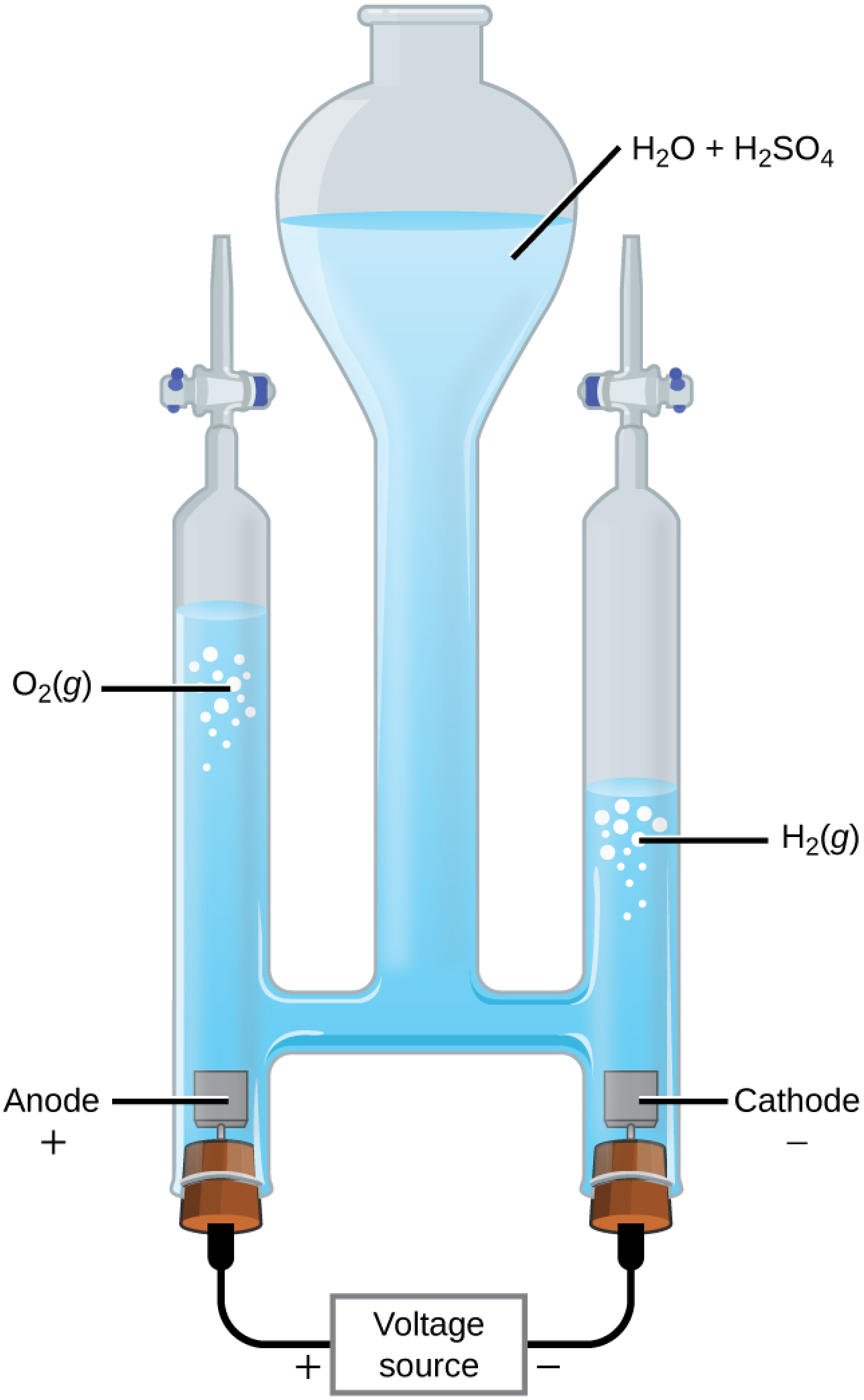

Figure 18.7b Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\begin{array}{llr} \text{(i) } 2\text{Cl}^-(aq) & \longrightarrow \text{Cl}_2(g) \;+\; 2\text{e}^- & E^\circ_{\text{anode}} = +1.358\text{ V} \\ \text{(ii) } 2\text{H}_2\text{O}(l) & \longrightarrow \text{O}_2(g) \;+\; 4\text{H}^+(aq) \;+\; 4\text{e}^- & E^\circ_{\text{anode}} = +1.229\text{ V} \end{array}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The **overpotential** is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\begin{array}{llr} \text{(iii) } 2\text{H}^+(aq) \;+\; 2\text{e}^- & \longrightarrow \text{H}_2(g) & E^\circ_{\text{cathode}} = 0.00\text{ V} \\ \text{(iv) } 2\text{H}_2\text{O}(l) \;+\; 2\text{e}^- & \longrightarrow \text{H}_2(g) \;+\; 2\text{OH}^-(aq) & E^\circ_{\text{cathode}} = -0.828\text{ V} \\ \text{(v) } \text{Na}^+(aq) \;+\; \text{e}^- & \longrightarrow \text{Na}(s) & E^\circ_{\text{cathode}} = -2.71\text{ V} \end{array}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only $1\times 10^{-7} M$. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$2\text{H}_2\text{O}(l) \;+\; 2\text{Cl}^-(aq) \longrightarrow \text{H}_2(g) \;+\; \text{Cl}_2(g) \;+\; 2\text{OH}^-(aq) \qquad E^\circ_{\text{cell}} = -2.186\text{ V}$$

As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

Electroplating

An important use for electrolytic cells is in **electroplating**. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chromeplated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure 18.7c).

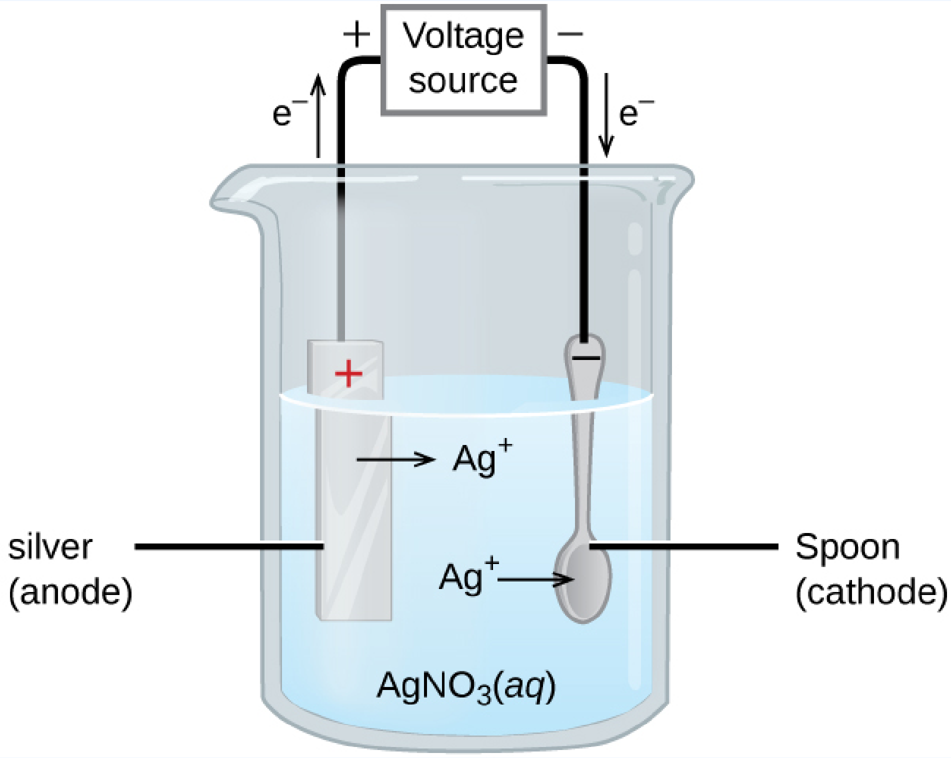

Figure 18.7c The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode (credit: *Chemistry (OpenStax)*, CC BY 4.0).

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\text{anode: Ag}(s) \longrightarrow \text{Ag}^{+}(aq) + \text{e}^{-}$$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\text{cathode: Ag}^{+}(aq) + \text{e}^{-} \longrightarrow \text{Ag}(s)$$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (*I*) is the ampere (A), which is the equivalent of 1 coulomb per second (1 A = 1 $\frac{\mathrm{C}}{\mathrm{s}}$). The total charge (*Q*, in coulombs) is given by

$$Q = I \times t = n \times F$$

Where *t* is the time in seconds, *n* the number of moles of electrons, and *F* is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example 18.7a

Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (*Q*) into moles of electrons (*n*). The charge is the current (*I*) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23\ \mathrm{C}}{\mathrm{s}} \times 1\ \mathrm{hr} \times \frac{60\ \mathrm{min}}{\mathrm{hr}} \times \frac{60\ \mathrm{s}}{\mathrm{min}}}{96,485\ \mathrm{C/mol}\backslash\mathrm{e}^-} = \frac{36,830\ \mathrm{C}}{96,485\ \mathrm{C/mol}\backslash\mathrm{e}^-} = 0.3817\ \mathrm{mol}\backslash\mathrm{e}^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } \mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)$$

The atomic mass of silver is 107.9 g/mol, so

$$\mathrm{mass}\backslash\mathrm{Ag} = 0.3817\ \mathrm{mol}\backslash\mathrm{e}^- \times \frac{1\ \mathrm{mol}\backslash\mathrm{Ag}}{1\ \mathrm{mol}\backslash\mathrm{e}^-} \times \frac{107.9\ \mathrm{g}\backslash\mathrm{Ag}}{1\ \mathrm{mol}\backslash\mathrm{Ag}} = 41.19\ \mathrm{g}\backslash\mathrm{Ag}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Exercise 18.7a

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Check Your Answer[1]

Example 18.7b

Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution

This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume} = (0.010 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}}) \times (3.3 \text{ m}^2 \times (\frac{10,000 \text{ cm}^2}{1 \text{ m}^2})) = 33 \text{ cm}^3$$

Cubic centimetres were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass} = \text{volume} \times \text{density} = 33 \cancel{\text{cm}^3} \times \frac{7.19 \text{ g}}{\cancel{\text{cm}^3}} = 237 \text{ g}\backslash\text{Cr}$$

$$\text{mol}\backslash\text{Cr} = 237\ \text{g}\backslash\text{Cr}\ \times\ \frac{1\ \text{mol}\backslash\text{Cr}}{52.00\ \text{g}\backslash\text{Cr}} = 4.56\ \text{mol}\backslash\text{Cr}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56\ \text{mol}\backslash\text{Cr}\ \times\ \frac{3\ \text{mol}\backslash\text{e}^-}{1\ \text{mol}\backslash\text{Cr}}\ \times\ \frac{96485\ \text{C}}{\text{mol}\backslash\text{e}^-} = 1.32\ \times\ 10^6\ \text{C}$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32\ \times\ 10^6\ \text{C}}{33.46\ \text{C/s}} = 3.95\ \times\ 10^4\ \text{s} = 11.0\ \text{hr}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

Key Equations

- $Q = I \times t = n \times F$

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Notes

1. $\text{Al}^{3+}(aq) + 3\text{e}^- \longrightarrow \text{Al}(s)$; 7.77 mol Al = 210.0 g Al.

CHAPTER 18 - SUMMARY

18.1 – Redox Reactions and Oxidation Numbers

Redox reactions involves the transfer of electrons and are defined by changes in reactant oxidation numbers. The oxidation number represents the charge of an atom if it were in an ionic compound. There are general guidelines that can be followed to determine the oxidation number of each element in a redox reaction. Oxidation is the loss of electrons and reduction is the gain of electrons. Whatever is oxidized in the reaction is considered to be the reducing agent and whatever is reduced is considered to be the oxidizing agent.

18.2 Balancing Redox Reactions

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^+) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydrogen ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

18.3 – Galvanic Cells

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, ‖. The solid, liquid, or aqueous phases within a half-cell are separated by a single line, $|$. The phase and concentration of the various species is included after the species name. Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

18.4 – Electrode and Cell Potentials

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, $E°$, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 M for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

18.5 –Batteries and Fuel Cells

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

18.6 – Corrosion

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus "protects" the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The "protected" metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

18.7 – Electrolysis

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Attribution & References

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CHAPTER 18 - REVIEW

18.1 – Redox Reactions and Oxidation Numbers

1. Determine the oxidation states of the elements in the following compounds:
   a. NaI
   b. $GdCl_3$
   c. $LiNO_3$
   d. H_2Se
   e. Mg_2Si
   f. RbO_2, rubidium superoxide
   g. HF
2. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.
   a. H_3PO_4
   b. $Al(OH)_3$
   c. SeO_2
   d. KNO_2
   e. In_2S_3
   f. P_4O_6

   Check Answer: [1]
3. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.
   a. H_2SO_4
   b. $Ca(OH)_2$
   c. BrOH
   d. $ClNO_2$
   e. $TiCl_4$
   f. NaH
4. Determine which elements are oxidized and which are reduced in the following reactions:
   a. $2Na(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2(g)$
   b. $Mg(s) + Cl_2(g) \rightarrow MgCl_2(aq)$
   c. $K_3P(s) + 2O_2(g) \rightarrow K_3PO_4(s)$

   Check Answer: [2]

5. Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:
    1. $Mg(s) + NiCl_2(aq) \rightarrow MgCl_2(aq) + Ni(s)$
    2. $PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$
    3. $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
    4. $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$
    5. $2K_2S_2O_3(s) + I_2(s) \rightarrow 2K_2S_4O_6(s) + 2KI(s)$

18.2 – Balancing Redox Reactions

1. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):
    a. $Sn^{4+}(aq) \rightarrow Sn^{2+}(aq)$
    b. $[Ag(NH_3)_2]^{+}(aq) \rightarrow Ag(s) + NH_3(aq)$
    c. $Hg_2Cl_2(s) \rightarrow Hg(l) + Cl^{-}(aq)$
    d. $H_2O(l) \rightarrow O_2(g)$ (in acidic solution)
    e. $IO_3^{-}(aq) \rightarrow I_2(s)$
    f. $SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$ (in acidic solution)
    g. $MnO_4^{-}(aq) \rightarrow Mn^{2+}(aq)$ (in acidic solution)
    h. $Cl^{-}(aq) \rightarrow ClO_3^{-}(aq)$ (in basic solution)**Check Answer:** [3]
2. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):
    a. $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq)$
    b. $Hg(l) + Br^{-}(aq) \rightarrow HgBr_4^{2-}(aq)$
    c. $ZnS(s) \rightarrow Zn(s) + S^{2-}(aq)$
    d. $H_2(g) \rightarrow H_2O(l)$ (in basic solution)
    e. $H_2(g) \rightarrow H_3O^{+}(aq)$ (in acidic solution)
    f. $NO_3^{-}(aq) \rightarrow HNO_2(aq)$ (in acidic solution)
    g. $MnO_2(s) \rightarrow MnO_4^{-}(aq)$ (in basic solution)
    h. $Cl^{-}(aq) \rightarrow ClO_3^{-}(aq)$ (in acidic solution)
3. Balance each of the following equations according to the half-reaction method:
    a. $Sn^{2+}(aq) + Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + Cu^{+}(aq)$
    b. $H_2S(g) + Hg_2^{2+}(aq) \rightarrow Hg(l) + S(s)$ (in acid)
    c. $CN^{-}(aq) + ClO_2(aq) \rightarrow CNO^{-}(aq) + Cl^{-}(aq)$ (in acid)
    d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$
    e. $HBrO(aq) \rightarrow Br^{-}(aq) + O_2(g)$ (in acid)

    Check Answer: [4]
4. Balance each of the following equations according to the half-reaction method:
    a. $Zn(s) + NO_3^{-}(aq) \rightarrow Zn^{2+}(aq) + N_2(g)$ (in acid)

   b. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + NH_3(aq)$ (in base)
   c. $CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+} + S(s) + NO(g)$ (in acid)
   d. $NH_3(aq) + O_2(g) \rightarrow NO_2(g)$ (gas phase)
   e. $Cl_2(g) + OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$ (in base)
   f. $H_2O_2(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + O_2(g)$ (in acid)
   g. $NO_2(g) \rightarrow NO_3^-(aq) + NO_2^-(aq)$ (in base)
   h. $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$
5. Balance each of the following equations according to the half-reaction method:
   a. $MnO_4^-(aq) + NO_2^-(aq) \rightarrow MnO_2(s) + NO_3^-(aq)$ (in base)
   b. $MnO_4^{2-}(aq) \rightarrow MnO_4^-(aq) + MnO_2(s)$ (in base)
   c. $Br_2(l) + SO_2(g) \rightarrow Br^-(aq) + SO_4^{2-}(aq)$ (in acid)

   Check Answer: [5]

18.3 – Galvanic Cells

1. Write the following balanced reactions using cell notation. Use platinum as an inert electrode, if needed.

   (a) $\text{Mg}(s) \ + \ \text{Ni}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) \ + \ \text{Ni}(s)$
   (b) $2\text{Ag}^{+}(aq) \ + \ \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) \ + \ 2\text{Ag}(s)$
   (c) $\text{Mn}(s) \ + \ \text{Sn}(\text{NO}_3)_2(aq) \longrightarrow \text{Mn}(\text{NO}_3)_2(aq) \ + \ \text{Au}(s)$
   (d) $3\text{CuNO}_3(aq) \ + \ \text{Au}(\text{NO}_3)_3(aq) \longrightarrow 3\text{Cu}(\text{NO}_3)_2(aq) \ + \ \text{Au}(s)$

   Check Answer: [6]
2. Given the following cell notations, determine the species oxidized, species reduced, and the oxidizing agent and reducing agent, without writing the balanced reactions.(a) $\text{Mg}(s)|\text{Mg}^{2+}(aq)||\text{Cu}^{2+}(aq)|\text{Cu}(s)$(b) $\text{Ni}(s)|\text{Ni}^{2+}(aq)||\text{Ag}^{+}(aq)|\text{Ag}(s)$
3. For the cell notations in the previous problem, write the corresponding balanced reactions.

   Check Answer: [7]
4. Balance the following reactions and write the reactions using cell notation. Ignore any inert electrodes, as they are never part of the half-reactions.

   (a) $\text{Al}(s) \ + \ \text{Zr}^{4+}(aq) \longrightarrow \text{Al}^{3+}(aq) \ + \ \text{Zr}(s)$
   (b) $\text{Ag}^{+}(aq) \ + \ \text{NO}(g) \longrightarrow \text{Ag}(s) \ + \ \text{NO}_3{}^{-}(aq)$ (acidic solution)
   (c) $\text{SiO}_3{}^{2-}(aq) \ + \ \text{Mg}(s) \longrightarrow \text{Si}(s) \ + \ \text{Mg(OH)}_2(s)$ (basic solution)
   (d) $\text{ClO}_3{}^{-}(aq) \ + \ \text{MnO}_2(s) \longrightarrow \text{Cl}^{-}(aq) \ + \ \text{MnO}_4{}^{-}(aq)$ (basic solution)
5. Identify the species oxidized, species reduced, and the oxidizing agent and reducing agent for all the reactions in the previous problem.

   Check Answer: [8]

6. From the information provided, use cell notation to describe the following systems:(a) In one half-cell, a solution of $Pt(NO_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $Cu(NO_3)_2$ solution with all solute concentrations 1 *M*.(b) The cathode consists of a gold electrode in a 0.55 *M* $Au(NO_3)_3$ solution and the anode is a magnesium electrode in 0.75 *M* $Mg(NO_3)_2$ solution.(c) One half-cell consists of a silver electrode in a 1 *M* $AgNO_3$ solution, and in the other half-cell, a copper electrode in 1 *M* $Cu(NO_3)_2$ is oxidized.
7. Why is a salt bridge necessary in galvanic cells like the one in Figure 18.3b?
   Check Answer: [9]
8. An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode part of the anode or cathode? Explain.
9. An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode part of the anode or cathode? Explain. **Check Answer:** [10]
10. The mass of three different metal electrodes, each from a different galvanic cell, were determined before and after the current generated by the oxidation-reduction reaction in each cell was allowed to flow for a few minutes. The first metal electrode, given the label A, was found to have increased in mass; the second metal electrode, given the label B, did not change in mass; and the third metal electrode, given the label C, was found to have lost mass. Make an educated guess as to which electrodes were active and which were inert electrodes, and which were anode(s) and which were the cathode(s).

18.4 – Electrode and Cell Potentials

1. For each reaction listed, determine its standard cell potential at 25 °C and whether the reaction is spontaneous at standard conditions.

   (a) $\mathrm{Mg}(s) \ + \ \mathrm{Ni}^{2+}(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) \ + \ \mathrm{Ni}(s)$
   (b) $2\mathrm{Ag}^{+}(aq) \ + \ \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) \ + \ 2\mathrm{Ag}(s)$
   (c) $\mathrm{Mn}(s) \ + \ \mathrm{Sn(NO_3)_2}(aq) \longrightarrow \mathrm{Mn(NO_3)_2}(aq) \ + \ \mathrm{Sn}(s)$
   (d) $3\mathrm{Fe(NO_3)_2}(aq) \ + \ \mathrm{Au(NO_3)_3}(aq) \longrightarrow 3\mathrm{Fe(NO_3)_3}(aq) \ + \ \mathrm{Au}(s)$
   Check Answer: [11]
2. For each reaction listed, determine its standard cell potential at 25 °C and whether the reaction is spontaneous at standard conditions.

   (a) $\mathrm{Mn}(s) \ + \ \mathrm{Ni}^{2+}(aq) \longrightarrow \mathrm{Mn}^{2+}(aq) \ + \ \mathrm{Ni}(s)$
   (b) $3\mathrm{Cu}^{2+}(aq) \ + \ 2\mathrm{Al}(s) \longrightarrow 2\mathrm{Al}^{3+}(aq) \ + \ 2\mathrm{Cu}(s)$
   (c) $\mathrm{Na}(s) \ + \ \mathrm{LiNO_3}(aq) \longrightarrow \mathrm{NaNO_3}(aq) \ + \ \mathrm{Li}(s)$
   (d) $\mathrm{Ca(NO_3)_2}(aq) \ + \ \mathrm{Ba}(s) \longrightarrow \mathrm{Ba(NO_3)_2}(aq) \ + \ \mathrm{Ca}(s)$
3. Determine the overall reaction and its standard cell potential at 25 °C for this reaction. Is the reaction

spontaneous at standard conditions?

$\text{Cu}(s)|\text{Cu}^{2+}(aq)||\text{Au}^{3+}(aq)|\text{Au}(s)$

Check Answer: [12]

4. Determine the overall reaction and its standard cell potential at 25 °C for the reaction involving the galvanic cell made from a half-cell consisting of a silver electrode in 1 *M* silver nitrate solution and a half-cell consisting of a zinc electrode in 1 *M* zinc nitrate. Is the reaction spontaneous at standard conditions?
5. Determine the overall reaction and its standard cell potential at 25 °C for the reaction involving the galvanic cell in which cadmium metal is oxidized to 1 *M* cadmium(II) ion and a half-cell consisting of an aluminum electrode in 1 *M* aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

   Check Answer: [13]
6. Determine the overall reaction and its standard cell potential at 25 °C for these reactions. Is the reaction spontaneous at standard conditions? Assume the standard reduction for $Br_2(l)$ is the same as for $Br_2(aq)$.

   $\text{Pt}(s)|\text{H}_2(g)|\text{H}^+(aq)||\text{Br}_2(aq)|\text{Br}^-(aq)|\text{Pt}(s)$

18.5 – Batteries and Fuel Cells

1. What are the desirable qualities of an electric battery?
2. List some things that are typically considered when selecting a battery for a new application.

   Check Answer: [14]
3. Consider a battery made from one half-cell that consists of a copper electrode in 1 *M* $CuSO_4$ solution and another half-cell that consists of a lead electrode in 1 *M* $Pb(NO_3)_2$ solution.(a) What are the reactions at the anode, cathode, and the overall reaction?(b) What is the standard cell potential for the battery?(c) Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.(d) Suppose sulfuric acid is added to the half-cell with the lead electrode and some $PbSO_4(s)$ forms. Would the cell potential increase, decrease, or remain the same?
4. Consider a battery with the overall reaction:

   $\text{Cu}(s) + 2\text{Ag}^+(aq) \longrightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(aq).$

   (a) What is the reaction at the anode and cathode?

   (b) A battery is "dead" when it has no cell potential. What is the value of *Q* when this battery is dead?

   (c) If a particular dead battery was found to have $[Cu^{2+}]$ = 0.11 *M*, what was the concentration of silver ion?

   Check Answer: [15]
5. An inventor proposes using a SHE (standard hydrogen electrode) in a new battery for smartphones that

also removes toxic carbon monoxide from the air:

$$\begin{array}{lllr}
\text{Anode:} & CO(g) + H_2O(l) & CO_2(g) + 2H^+(aq) + 2e^- & E^\circ_{\text{anode}} = -0.53\text{ V} \\
\text{Cathode:} & 2H^+(aq) + 2e^- & H_2(g) & E^\circ_{\text{cathode}} = 0\text{ V} \\
\hline
\text{Overall:} & CO(g) + H_2O(l) & CO_2(g) + H_2(g) & E^\circ_{\text{cell}} = +0.53\text{ V}
\end{array}$$

Would this make a good battery for smartphones? Why or why not?

6. Why do batteries go dead, but fuel cells do not? **Check Answer:** [16]
7. Explain what happens to battery voltage as a battery is used, in terms of the Nernst equation.
8. Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures. **Check Answer:** [17]

18.6 – Corrosion

1. Which member of each pair of metals is more likely to corrode (oxidize)?(a) Mg or Ca(b) Au or Hg(c) Fe or Zn(d) Ag or Pt
2. Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is mostly iron, so use −0.447 V as the standard reduction potential for steel.
   Check Answer: [18]
3. Aluminum $\left(E^\circ_{Al^{3+}/Al} = -2.07\text{ V}\right)$ is more easily oxidized than iron $\left(E^\circ_{Fe^{3+}/Fe} = -0.477\text{ V}\right)$, and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. Explain this observation.
4. If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.
   Check Answer: [19]
5. Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?
6. Why would a sacrificial anode made of lithium metal be a bad choice despite its $E^\circ_{Li^+/Li} = -3.04\text{ V}$, which appears to be able to protect all the other metals listed in the standard reduction potential table?
   Check Answer: [20]

18.7 – Electrolysis

1. Identify the reaction at the anode, reaction at the cathode, the overall reaction, and the approximate potential required for the electrolysis of the following molten salts. Assume standard states and that the standard reduction potentials in Appendix M are the same as those at each of the melting points. Assume the efficiency is 100%.
   (a) $CaCl_2$
   (b) LiH
   (c) $AlCl_3$
   (d) $CrBr_3$
2. What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of 3.33×10^5 C passes through each cell? Assume the voltage is sufficient to perform the reduction.
   Check Answer: [21]
3. How long would it take to reduce 1 mole of each of the following ions using the current indicated? Assume the voltage is sufficient to perform the reduction.(a) Al^{3+}, 1.234 A(b) Ca^{2+}, 22.2 A(c) Cr^{5+}, 37.45 A(d) Au^{3+}, 3.57 A
4. A current of 2.345 A passes through the cell shown in Figure 18.7b for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? Assume the voltage is sufficient to perform the reduction. (Hint: Is hydrogen the only gas present above the water?)
   Check Answer: [22]
5. An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a $Zn(NO_3)_2$ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm^3. Assume the efficiency is 100%.

Attribution & References

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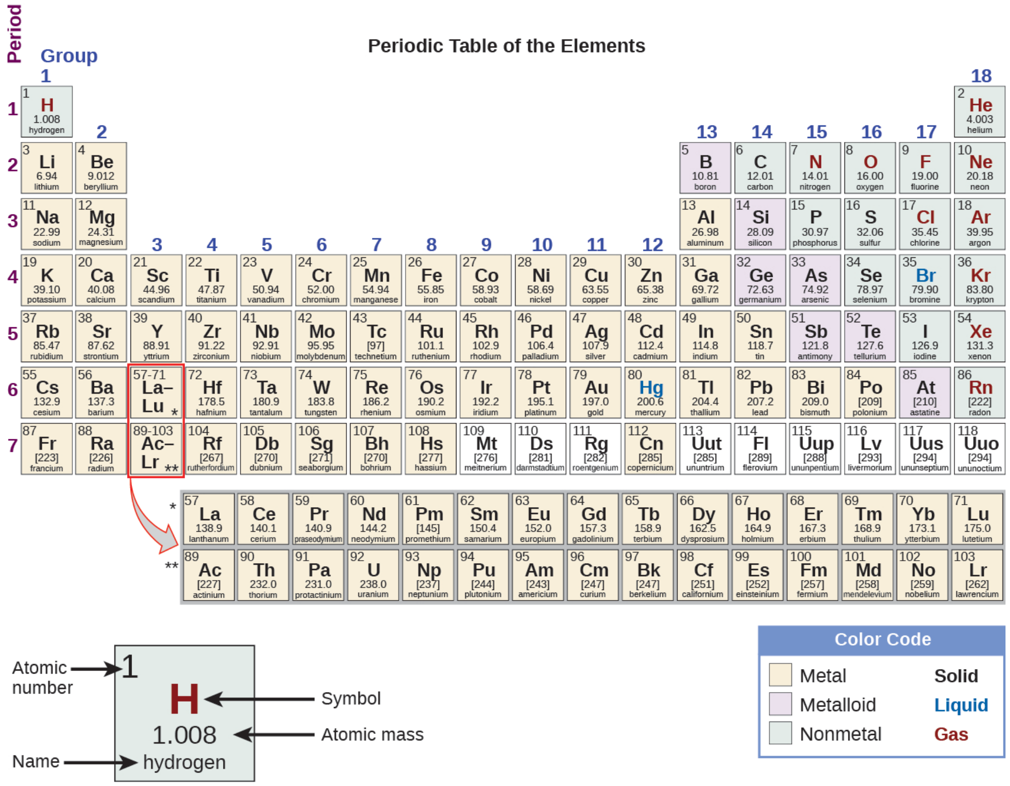
Notes

1. (a) H +1, P +5, O −2; (b) Al +3, H +1, O −2; (c) Se +4, O −2; (d) K +1, N +3, O −2; (e) In +3, S −2; (f) P +3, O −2
2. (a) Na is oxidized, H^+ is reduced; (b) Mg is oxidized, Cl_2 is reduced; (c) P^{3-} is oxidized, O_2 is reduced;
3. (a)$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ (b)$[Ag(NH_3)_2]^+(aq) + e^- \rightarrow Ag(s) + 2NH_3(aq)$ (c) $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$ (d) $2H_2O(l) \rightarrow O_2 + 4H^+(aq) + 4e^-$ (e) $6H_2O(l) + 2IO_3^-(aq) + 10e^- \rightarrow I_2(s) + 12OH^-(aq)$ (f) $H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$ (g) $8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ (a) $Cl^-(aq) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$
4. (a) $Sn^{2+}(aq) + 2Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2Cu^+(aq)$ (b) $H_2S(g) + Hg_2^{2+}(aq) + 2H_2O(l) \rightarrow 2Hg(l) + S(s) + 2H_3O^+(aq)$ (c) $5CN^-(aq) + 2ClO_2(aq) + 3H_2O(l) \rightarrow 5CNO^-(aq) + 2Cl^-(aq) + 2H_3O^+(aq)$ (d)$Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$ (e) $2HBrO(aq) + 2H_2O(l) \rightarrow 2H_3O(aq) + 2Br^-(aq) + O_2(g)$
5. (a) $2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$ (b) $3MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_4^-(aq) + 4OH^-(aq) + MnO_2(s)$ (in base) (c) $Br_2(l) + SO_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 2Br^-(aq) + SO_4^{2-}(aq)$
6. (a) $\text{Mg}(s)|\text{Mg}^{2+}(aq)\|\text{Ni}^{2+}(aq)|\text{Ni}(s)$; (b) $\text{Cu}(s)|\text{Cu}^{2+}(aq)\|\text{Ag}^{+}(aq)|\text{Ag}(s)$; (c) $\text{Mn}(s)|\text{Mn}^{2+}(aq)\|\text{Sn}^{2+}(aq)|\text{Sn}(s)$; (d) $\text{Pt}(s)|\text{Cu}^{+}(aq),\backslash;\text{Cu}^{2+}(aq)\|\text{Au}^{3+}(aq)|\text{Au}(s)$
7. (a) $\text{Mg}(s)\ +\ \text{Cu}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq)\ +\ \text{Cu}(s)$; (b) $2\text{Ag}^{+}(aq)\ +\ \text{Ni}(s) \longrightarrow \text{Ni}^{2+}(aq)\ +\ 2\text{Ag}(s)$
8. Species oxidized = reducing agent: (a) Al(*s*); (b) NO(*g*); (c) Mg(*s*); and (d) $MnO_2(s)$; Species reduced = oxidizing agent: (a) $Zr^{4+}(aq)$; (b) $Ag^+(aq)$; (c) $\text{SiO}_3{}^{2-}(aq)$; and (d) $\text{ClO}_3{}^{-}(aq)$
9. Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.
10. Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.
11. (a) +2.115 V (spontaneous); (b) +0.4626 V (spontaneous); (c) +1.0589 V (spontaneous); (d) +0.727 V (spontaneous)
12. $3\text{Cu}(s)\ +\ 2\text{Au}^{3+}(aq) \longrightarrow 3\text{Cu}^{2+}(aq)\ +\ 2\text{Au}(s)$; +1.16 V; spontaneous
13. $3\text{Cd}(s)\ +\ 2\text{Al}^{3+}(aq) \longrightarrow 3\text{Cd}^{2+}(aq)\ +\ 2\text{Al}(s)$; −1.259 V; nonspontaneous
14. Considerations include: cost of the materials used in the battery, toxicity of the various components (what constitutes proper disposal), should it be a primary or secondary battery, energy requirements (the "size" of the battery/how long should it last), will a particular battery leak when the new device is used according to directions, and its mass (the total mass of the new device).
15. (a) [latex]\begin{array}{lr @{{}\longrightarrow{}} ll} \text{anode:} & \text{Cu}(s) & \longrightarrow \text{Cu}^{2+}(aq)\;+\;2\text{e}^{-} & E_{\text{anode}}^{\circ} = 0.34\;\text{V} \\[0.5em] \text{cathode:} & 2\;\times\;(\text{Ag}^{+}(aq)\;+\;\text{e}^{-} & \longrightarrow \text{Ag}(s)) & E_{\text{cathode}}^{\circ} = 0.7996\;\text{V} \end{array}[/latex]
16. Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.
17. E_{cell}, as described in the Nernst equation, has a term that is directly proportional to temperature. At low temperatures, this term is decreased, resulting in a lower cell voltage provided by the battery to the device—the same effect as a battery

running dead.

18. Mg and Zn
19. Both examples involve cathodic protection. The (sacrificial) anode is the metal that corrodes (oxidizes or reacts). In the case of iron (−0.447 V) and zinc (−0.7618 V), zinc has a more negative standard reduction potential and so serves as the anode. In the case of iron and copper (0.34 V), iron has the smaller standard reduction potential and so corrodes (serves as the anode).
20. While the reduction potential of lithium would make it capable of protecting the other metals, this high potential is also indicative of how reactive lithium is; it would have a spontaneous reaction with most substances. This means that the lithium would react quickly with other substances, even those that would not oxidize the metal it is attempting to protect. Reactivity like this means the sacrificial anode would be depleted rapidly and need to be replaced frequently. (Optional additional reason: fire hazard in the presence of water.)
21. (a) $\begin{array}{ll} \text{mass Ca} & 69.1\text{ g} \\ \text{mass Cl}_2 & 122\text{ g} \end{array}$ (b) $\begin{array}{ll} \text{mass Li} & 23.9\text{ g} \\ \text{mass H}_2 & 3.48\text{ g} \end{array}$ (c) $\begin{array}{ll} \text{mass Al} & 31.0\text{ g} \\ \text{mass Cl}_2 & 122\text{ g} \end{array}$ (d) $\begin{array}{ll} \text{mass Cr} & 59.8\text{ g} \\ \text{mass Br}_2 & 276\text{ g} \end{array}$
22. 0.79 L

APPENDIX A: THE PERIODIC TABLE



Periodic Table of the Elements

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008 hydrogen																	2 He 4.003 helium
2	3 Li 6.94 lithium	4 Be 9.012 beryllium											5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La– Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac– Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Uut [285] ununtrium	114 Fl [289] flerovium	115 Uup [288] ununpentium	116 Lv [293] livermorium	117 Uus [294] ununseptium	118 Uuo [294] ununoctium

*	57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
**	89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium

Color Code	
Metal	Solid
Metalloid	Liquid
Nonmetal	Gas

Graphical version of the periodic table of the elements. The 18 columns are labeled “Group” and the 7 rows are labeled “Period.” Below the table to the right is a box labeled “Color Code” with different colors for metals, metalloids, and nonmetals, as well as solids, liquids, and gases. To the left of this box is an enlarged picture of the upper-left most box on the table. The number 1 is in its upper-left hand corner and is labeled “Atomic number.” The letter “H” is in the middle in red indicating that it is a gas. It is labeled “Symbol.” Below that is the number 1.008 which is labeled “Atomic Mass.” Below that is the word hydrogen which is labeled “name.” The color of the box indicates that it is a nonmetal. Each element will be described in this order: atomic number; name; symbol; whether it is a metal, metalloid, or nonmetal; whether it is a solid, liquid, or gas; and atomic mass.

Below, please find the periodic table of the elements in table/text format.

Periodic Table of Elements in Tabular Format

Period (Row)	Group (Column)	Atomic Number	Symbol	Name	Atomic Mass	State of Matter at Room Temperature	Type of Element	Family	Common Ion	Valence Electrons	Outer Shell Electron Configuration	Electronegativity Values
1	1	1	H	Hydrogen	1.008	gas	nonmetal	–	H^+	1	$1s^1$	2.1
1	18	2	He	Helium	4.003	gas	nonmetal	Noble gas	no ion	2	$1s^2$	–
2	1	3	Li	Lithium	6.94	solid	metal	Alkali metal	Li^+	1	$2s^1$	1.0
2	2	4	Be	Beryllium	9.01	solid	metal	Alkaline earth metal	Be^{2+}	2	$2s^2$	1.5
2	13	5	B	Boron	10.81	solid	metalloid	–		3	$2s^22p^1$	2.0
2	14	6	C	Carbon	12.01	solid	nonmetal	–	C^{4-}	4	$2s^22p^2$	2.5
2	15	7	N	Nitrogen	14.01	gas	nonmetal	Pnictogen	N^{3-}	5	$2s^22p^3$	3.0
2	16	8	O	Oxygen	16.00	gas	nonmetal	Chalcogen	O^{2-}	6	$2s^22p^4$	3.5
2	17	9	F	Fluorine	19.00	gas	nonmetal	Halogen	F^-	7	$2s^22p^5$	4.0
2	18	10	Ne	Neon	20.18	gas	nonmetal	Noble gas	no ion	8	$2s^22p^6$	–
3	1	11	Na	Sodium	22.99	solid	metal	Alkali metal	Na^+	1	$3s^1$	0.9
3	2	12	Mg	Magnesium	24.30	solid	metal	Alkaline earth metal	Mg^{2+}	2	$3s^2$	1.2
3	13	13	Al	Aluminum	26.98	solid	metal	–	Al^{3+}	3	$3s^23p^1$	1.5
3	14	14	Si	Silicon	28.08	solid	metalloid	–		4	$3s^23p^2$	1.8
3	15	15	P	Phosphorus	30.97	solid	nonmetal	Pnictogen	P^{3-}	5	$3s^23p^3$	2.1
3	16	16	S	Sulfur	32.06	solid	nonmetal	Chalcogen	S^{2-}	6	$3s^23p^4$	2.5
3	17	17	Cl	Chlorine	35.45	gas	nonmetal	Halogen	Cl^-	7	$3s^23p^5$	3.0
3	18	18	Ar	Argon	39.79	gas	nonmetal	Noble gas	no ion	8	$3s^23p^6$	–
4	1	19	K	Potassium	39.10	solid	metal	Alkali metal	K^+	1	$4s^1$	0.8
4	2	20	Ca	Calcium	40.08	solid	metal	Alkaline earth metal	Ca^{2+}	2	$4s^2$	1.0
4	3	21	Sc	Scandium	44.96	solid	metal	Transition metal			$4s^23d^1$	1.3
4	4	22	Ti	Titanium	47.87	solid	metal	Transition metal			$4s^23d^2$	1.5
4	5	23	V	Vanadium	50.94	solid	metal	Transition metal			$4s^23d^3$	1.6
4	6	24	Cr	Chromium	52.00	solid	metal	Transition metal	Cr^{3+} Cr^{6+}		$4s^13d^5$	1.6
4	7	25	Mn	Manganese	54.94	solid	metal	Transition metal	Mn^{2+}		$4s^23d^5$	1.5
4	8	26	Fe	Iron	55.85	solid	metal	Transition metal	Fe^{2+} Fe^{3+}		$4s^23d^6$	1.8
4	9	27	Co	Cobalt	58.93	solid	metal	Transition metal	Co^{2+}		$4s^23d^7$	1.9
4	10	28	Ni	Nickel	58.69	solid	metal	Transition metal	Ni^{2+}		$4s^23d^8$	1.9
4	11	29	Cu	Copper	63.55	solid	metal	Transition metal	Cu^+ Cu^{2+}		$4s^13d^{10}$	1.9
4	12	30	Zn	Zinc	65.38	solid	metal	Transition metal	Zn^{2+}		$4s^23d^{10}$	1.6
4	13	31	Ga	Gallium	69.72	solid	metal	–			$4s^23d^{10}4p^1$	1.6
4	14	32	Ge	Germanium	72.63	solid	metalloid	–			$4s^23d^{10}4p^2$	1.8
4	15	33	As	Arsenic	74.92	solid	metalloid	Pnictogen	As^{3-}		$4s^23d^{10}4p^3$	2.0
4	16	34	Se	Selenium	78.97	solid	nonmetal	Chalcogen	Se^{2-}		$4s^23d^{10}4p^4$	2.4
4	17	35	Br	Bromine	79.90	liquid	nonmetal	Halogen	Br^-		$4s^23d^{10}4p^5$	2.8
4	18	36	Kr	Krypton	83.80	gas	nonmetal	Noble gas	no ion		$4s^23d^{10}4p^6$	–
5	1	37	Rb	Rubidium	85.47	solid	metal	Alkali metal	Rb^+		$5s^1$	0.8
5	2	38	Sr	Strontium	87.62	solid	metal	Alkaline earth metal	Sr^{2+}		$5s^2$	1.0

Period (Row)	**Group (Column)**	**Atomic Number**	**Symbol**	**Name**	**Atomic Mass**	**State of Matter at Room Temperature**	**Type of Element**	**Family**	**Common Ion**	**Valence Electrons**	**Outer Shell Electron Configuration**	**Electronegativity Values**
5	3	39	Y	Yttrium	88.91	solid	metal	Transition metal			$5s^24d^1$	1.2
5	4	40	Zr	Zirconium	91.22	solid	metal	Transition metal			$5s^24d^2$	1.4
5	5	41	Nb	Niobium	92.91	solid	metal	Transition metal			$5s^14d^4$	1.6
5	6	42	Mo	Molybdenum	95.95	solid	metal	Transition metal			$5s^14d^5$	1.8
5	7	43	Tc	Technetium	98.91	solid	metal	Transition metal			$5s^14d^6$	1.9
5	8	44	Ru	Ruthenium	101.1	solid	metal	Transition metal			$5s^14d^7$	2.2
5	9	45	Rh	Rhodium	102.9	solid	metal	Transition metal			$5s^14d^8$	2.2
5	10	46	Pd	Palladium	106.4	solid	metal	Transition metal	Ag^+		$4d^{10}$	2.2
5	11	47	Ag	Silver	107.9	solid	metal	Transition metal	Cd^{2+}		$5s^14d^{10}$	1.9
5	12	48	Cd	Cadmium	112.4	solid	metal	Transition metal			$5s^24d^{10}$	1.7
5	13	49	In	Indium	114.8	solid	metal	–			$5s^24d^{10}5p^1$	1.7
5	14	50	Sn	Tin	118.7	solid	metal	–			$5s^24d^{10}5p^2$	1.8
5	15	51	Sb	Antimony	121.8	solid	metalloid	Pnictogen			$5s^24d^{10}5p^3$	1.9
5	16	52	Te	Tellurium	127.6	solid	metalloid	Chalcogen	Te^{2-}		$5s^24d^{10}5p^4$	2.1
5	17	53	I	Iodine	126.9	solid	nonmetal	Halogen	I^-		$5s^24d^{10}5p^5$	2.5
5	18	54	Xe	Xenon	131.3	gas	nonmetal	Noble gas	no ion		$5s^24d^{10}5p^6$	–
6	1	55	Cs	Cesium	132.9	solid	metal	Alkali metal	Cs^+		$6s^1$	0.7
6	2	56	Ba	Barium	137.3	solid	metal	Alkaline earth metal	Ba^{2+}		$6s^2$	0.9
6	3	57	La	Lanthanum	138.9	solid	metal	Lanthanide			$6s^25d^1$	1.0-1.2
6	n/a	58	Ce	Cerium	140.1	solid	metal	Lanthanide			$6s^24f^2$	1.0-1.2
6	n/a	59	Pr	Praseodymium	140.9	solid	metal	Lanthanide			$6s^24f^3$	1.0-1.2
6	n/a	60	Nd	Neodymium	144.2	solid	metal	Lanthanide			$6s^24f^4$	1.0-1.2
6	n/a	61	Pm	Promethium	145.0	solid	metal	Lanthanide			$6s^24f^5$	1.0-1.2
6	n/a	62	Sm	Samarium	150.4	solid	metal	Lanthanide			$6s^24f^6$	1.0-1.2
6	n/a	63	Eu	Europium	152.0	solid	metal	Lanthanide			$6s^24f^7$	1.0-1.2
6	n/a	64	Gd	Gadolinium	157.3	solid	metal	Lanthanide			$6s^24f^75d^1$	1.0-1.2
6	n/a	65	Tb	Terbium	158.9	solid	metal	Lanthanide			$6s^24f^9$	1.0-1.2
6	n/a	66	Dy	Dysprosium	162.5	solid	metal	Lanthanide			$6s^24f^{10}$	1.0-1.2
6	n/a	67	Ho	Holmium	164.9	solid	metal	Lanthanide			$6s^24f^{11}$	1.0-1.2
6	n/a	68	Er	Erbium	167.3	solid	metal	Lanthanide			$6s^24f^{12}$	1.0-1.2
6	n/a	69	Tm	Thulium	168.9	solid	metal	Lanthanide			$6s^24f^{13}$	1.0-1.2

Period (Row)	**Group (Column)**	**Atomic Number**	**Symbol**	**Name**	**Atomic Mass**	**State of Matter at Room Temperature**	**Type of Element**	**Family**	**Common Ion**	**Valence Electrons**	**Outer Shell Electron Configuration**	**Electronegativity Values**
6	n/a	70	Yb	Ytterbium	173.0	solid	metal	Lanthanide			$6s^2 4f^{14}$	1.0-1.2
6	n/a	71	Lu	Lutetium	175.0	solid	metal	Lanthanide			$6s^2 4f^{14} 5d^1$	1.0-1.2
6	4	72	Hf	Hafnium	178.5	solid	metal	Transition metal			$6s^2 4f^{14} 5d^2$	1.3
6	5	73	Ta	Tantalum	180.9	solid	metal	Transition metal			$6s^2 4f^{14} 5d^3$	1.5
6	6	74	W	Tungsten	183.8	solid	metal	Transition metal			$6s^2 4f^{14} 5d^4$	1.7
6	7	75	Re	Rhenium	186.2	solid	metal	Transition metal			$6s^2 4f^{14} 5d^5$	1.9
6	8	76	Os	Osmium	190.2	solid	metal	Transition metal			$6s^2 4f^{14} 5d^6$	2.2
6	9	77	Ir	Iridium	192.2	solid	metal	Transition metal			$6s^2 4f^{14} 5d^7$	2.2
6	10	78	Pt	Platinum	195.1	solid	metal	Transition metal	Pt^{2+}		$6s^1 4f^{14} 5d^9$	2.2
6	11	79	Au	Gold	197.0	solid	metal	Transition metal	Au^+ Au^{3+}		$6s^1 4f^{14} 5d^{10}$	2.4
6	12	80	Hg	Mercury	200.6	liquid	metal	Transition metal	Hg_2^{2+} Hg^{2+}		$6s^2 4f^{14} 5d^{10}$	1.9
6	13	81	Tl	Thallium	204.4	solid	metal	–			$6s^2 4f^{14} 5d^{10} 6p^1$	1.8
6	14	82	Pb	Lead	207.2	solid	metal	–			$6s^2 4f^{14} 5d^{10} 6p^2$	1.9
6	15	83	Bi	Bismuth	209.0	solid	metal	Pnictogen			$6s^2 4f^{14} 5d^{10} 6p^3$	1.9
6	16	84	Po	Polonium	209	solid	metal	Chalcogen			$6s^2 4f^{14} 5d^{10} 6p^4$	2.0
6	17	85	At	Astatine	210	solid	metalloid	Halogen	At^-		$6s^2 4f^{14} 5d^{10} 6p^5$	2.2
6	18	86	Rn	Radon	222	gas	nonmetal	Noble gas	no ion		$6s^2 4f^{14} 5d^{10} 6p^6$	–
7	1	87	Fr	Francium	223	solid	metal	Alkali metal	Fr^+		$7s^1$	0.7
7	2	88	Ra	Radium	226	solid	metal	Alkaline earth metal	Ra^{2+}		$7s^2$	0.9
7	3	89	Ac	Actinium	227	solid	metal	Actinide			$7s^2 6d^1$	1.1
7	n/a	90	Th	Thorium	232	solid	metal	Actinide			$7s^2 6d^2$	1.3
7	n/a	91	Pa	Protactinium	231	solid	metal	Actinide			$7s^2 5f^2 6d^1$	1.4
7	n/a	92	U	Uranium	238	solid	metal	Actinide			$7s^2 5f^3 6d^1$	1.4
7	n/a	93	Np	Neptunium	237	solid	metal	Actinide			$7s^2 5f^4 6d^1$	1.4-1.3
7	n/a	94	Pu	Plutonium	244	solid	metal	Actinide			$7s^2 5f^6$	1.4-1.3
7	n/a	95	Am	Americium	243	solid	metal	Actinide			$7s^2 5f^7$	1.4-1.3
7	n/a	96	Cm	Curium	247	solid	metal	Actinide			$7s^2 5f^7 6d^1$	1.4-1.3
7	n/a	97	Bk	Berkelium	247	solid	metal	Actinide			$7s^2 5f^8 6d^1$	1.4-1.3
7	n/a	98	Cf	Californium	251	solid	metal	Actinide			$7s^2 5f^{10}$	1.4-1.3
7	n/a	99	Es	Einsteinium	252	solid	metal	Actinide			$7s^2 5f^{11}$	1.4-1.3
7	n/a	100	Fm	Fermium	257	solid	metal	Actinide			$7s^2 5f^{12}$	1.4-1.3
7	n/a	101	Md	Mendelevium	258	solid	metal	Actinide			$7s^2 5f^{13}$	1.4-1.3
7	n/a	102	No	Nobelium	259	solid	metal	Actinide			$7s^2 5f^{14}$	1.4-1.3

Period (Row)	Group (Column)	Atomic Number	Symbol	Name	Atomic Mass	State of Matter at Room Temperature	Type of Element	Family	Common Ion	Valence Electrons	Outer Shell Electron Configuration	Electronegativity Values
7	n/a	103	Lr	Lawrencium	262	solid	metal	Actinide			$7s^2 5f^{14} 6d^1$	–
7	4	104	Rf	Rutherfordium	261	solid	metal	Transition metal			$7s^2 5f^{14} 6d^2$	–
7	5	105	Db	Dubnium	268	solid	metal	Transition metal			$7s^2 5f^{14} 6d^3$	–
7	6	106	Sg	Seaborgium	269	solid	metal	Transition metal			$7s^2 5f^{14} 6d^4$	–
7	7	107	Bh	Bohrium	270	solid	metal	Transition metal			$7s^2 5f^{14} 6d^5$	–
7	8	108	Hs	Hassium	269	solid	metal	Transition metal			$7s^2 5f^{14} 6d^6$	–
7	9	109	Mt	Meitnerium	277	unknown	unknown	Transition metal			$7s^2 5f^{14} 6d^7$	–
7	10	110	Ds	Darmstadtium	281	unknown	unknown	Transition metal			$7s^2 5f^{14} 6d^8$	–
7	11	111	Rg	Roentgenium	281	unknown	unknown	Transition metal			$7s^2 5f^{14} 6d^9$	–
7	12	112	Cn	Copernicium	285	solid	metal	Transition metal			$7s^2 5f^{14} 6d^{10}$	–
7	13	113	Nh	Nihonium	286	unknown	unknown	–				–
7	14	114	Fl	Flerovium	289	solid	metal	–				–
7	15	115	Mc	Moscovium	288	unknown	unknown	Pnictogen				–
7	16	116	Lv	Livermorium	293	unknown	unknown	Chalcogen				–
7	17	117	Ts	Tennessine	294	unknown	unknown	Halogen				–
7	18	118	Og	Oganesson	294	unknown	unknown	–				–

Links & Resources

Watch The Periodic Table: Crash Course Chemistry #4 (11:21 min)

Watch The Periodic Table Explained (3:06 min)

For suggestions on accessible periodic tables for those with low/no vision, visit:

- Accessible Periodic Table Options – Perkins School for the Blind
- Accessible Periodic Table of Elements – American Chemical Society (acs.org)
- Independence Science Periodic Table of the Elements

Low vision and braille versions of the periodic table are available.

Attribution & References

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- Figure 3 from "3.6 The Periodic Table", Figure 2 from "3.7 Molecular and Ionic Compounds", Figure 4 from "3.4 Electronic Structure of the Atoms (General configurations)", Figure 3 from "4.2 Covalent Bonding" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* .
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References

Injosoft. (2023). *List of chemical elements – periodic table*. Periodic Table of the Elements.
Periodic Table of the elements. (2023). www.periodictable.one.

APPENDIX B: ESSENTIAL MATHEMATICS

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$$\begin{array}{rl}
1000 & 1 \times 10^{3} \\
100 & 1 \times 10^{2} \\
10 & 1 \times 10^{1} \\
1 & 1 \times 10^{0} \\
0.1 & 1 \times 10^{-1} \\
0.001 & 1 \times 10^{-3} \\
2386 & 2.386 \times 1000 = 2.386 \times 10^{3} \\
0.123 & 1.23 \times 0.1 = 1.23 \times 10^{-1}
\end{array}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, $1,230,000,000 = 1.23 \times 10^{9}$, and $0.00000000036 = 3.6 \times 10^{-10}$.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example B.1

Adding Exponentials

Add 5.00 × 10^{-5} and 3.00 × 10^{-3}.

Solution

$$3.00 \times 10^{-3} = 300 \times 10^{-5}$$
$$(5.00 \times 10^{-5}) + (300 \times 10^{-5}) = 305 \times 10^{-5} = 3.05 \times 10^{-3}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example B.2

Subtracting Exponentials

Subtract 4.0 × 10^{-7} from 5.0 × 10^{-6}.

Solution

$$4.0 \times 10^{-7} = 0.40 \times 10^{-6}$$
$$(5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) = 4.6 \times 10^{-6}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Example B.3

Multiplying Exponentials

Multiply 4.2 × 10^{-8} by 2.0 × 10^{3}.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^{3}) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Example B.4

Dividing Exponentials

Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = (\frac{3.6}{6.0}) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Example B.5

Squaring Exponentials

Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2 \times (-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Example B.6

Cubing Exponentials

Cube the number 2×10^{4}.

Solution

$$(2 \times 10^4)^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Example B.7

Finding the Square Root of Exponentials

Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times \sqrt{10}^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

Example B.8

Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

$$\begin{array}{r} 4.38\underline{3}\ \text{g} \\ 0.002\underline{3}\ \text{g} \\ \hline 4.38\underline{5}\ \text{g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Example B.9

Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

$$0.623\underline{8} \ \times \ 6.\underline{6} = 4.\underline{1}$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Table B.1 Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.001	10^{-3}	−3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where *x* is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which *e* must be raised to equal the number; *e* is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^{x} (where *x* is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.
$$\log xy = \log x + \log y,\backslash;\text{and}\backslash;\ln xy = \ln x + \ln y$$
2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.
$$\log \frac{x}{y} = \log x - \log y,\backslash;\text{and}\backslash;\ln \frac{x}{y} = \ln x - \ln y$$
3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of

the number.

$$\log x^n = n\log x \text{ and\;}\ln x^n = n\ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Example B.10

Solving Quadratic Equations

Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution

Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (*x*–*y*) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (*x*), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (*y*).

When the value of *y* is changing as a function of *x* (that is, different values of *x* correspond to different values of *y*), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (*x*,*y*) data pairs.

Example B.11

Graphing the Dependence of *y* on *x*

Table B.2 X and Y values for Graph

x	*y*
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of *y* on *x*.

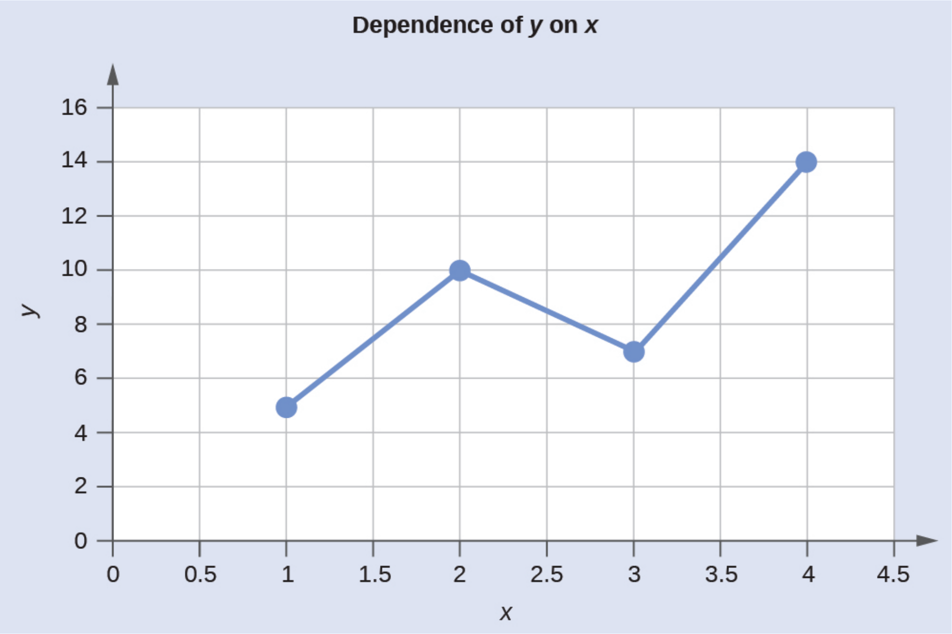

Figure B.1 XY graph of data in Table B.2

If the function that describes the dependence of *y* on *x* is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Example B.12

Plotting Data Pairs

If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

Table B.3 XY values

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18

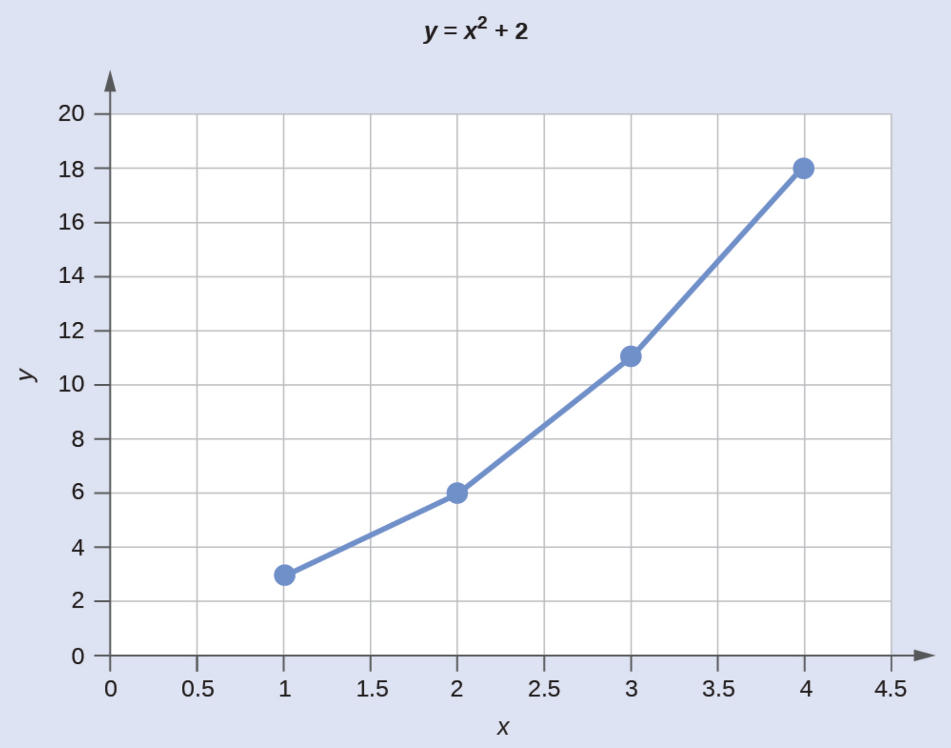

Figure B.2 XY graph of data in Table B.3

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APPENDIX C: UNITS AND CONVERSION FACTORS

Units of Length, Mass, Energy & Pressure

Table C.1 Units of Length

Unit	Equivalent Units
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)
centimeter (cm)	= 0.01 m (exact, definition)
millimeter (mm)	= 0.001 m (exact, definition)
kilometer (km)	= 1000 m (exact, definition)
angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
yard (yd)	= 0.9144 m
inch (in.)	= 2.54 cm (exact, definition)
mile (US)	= 1.60934 km

Table C.2 Units of Volume

Unit	Equivalent Units
liter (L)	= 0.001 m^3 (exact, definition) = 1000 cm^3 (exact, definition) = 1.057 (US) quarts
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm^3 (exact, definition)
microliter (μL)(μL)	= 10^{-6} L (exact, definition) = 10^{-3} cm^3 (exact, definition)
liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
dry quart	= 1.1012 L
cubic foot (US)	= 28.316 L

Table C.3 Units of Mass

Unit	Equivalent Units
gram (g)	= 0.001 kg (exact, definition)
milligram (mg)	= 0.001 g (exact, definition)
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb
ounce (oz) (avoirdupois)	= 28.35 g
pound (lb) (avoirdupois)	= 0.4535924 kg
ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Table C.4 Units of Energy

Unit	Equivalent Units
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[1]

Table C.5 Units of Pressure

Unit	Equivalent Units
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10^5 Pa (exact, definition) = 10^5 kg m^{-1} s^{-2} (exact, definition)

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Notes

1. BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

APPENDIX D: FUNDAMENTAL PHYSICAL CONSTANTS

Fundamental Physical Constants

Table D.1 Fundamental Physical constants

Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
Avogadro's number	6.0221367×10^{23} mol^{-1}
Boltzmann's constant (k)	1.380658×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
electron charge (e)	$1.60217733 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093897 \times 10^{-31}$ kg
Faraday's constant (F)	9.6485309×10^{4} C mol^{-1}
gas constant (R)	8.205784×10^{-2} L atm mol^{-1} K^{-1} = 8.314510 J mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 0 °C	22.41409 L mol^{-1}
molar volume of an ideal gas, 1 bar, 0 °C	22.71108 L mol^{-1}
neutron rest mass (m_n)	$1.6749274 \times 10^{-27}$ kg
Planck's constant (h)	$6.6260755 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726231 \times 10^{-27}$ kg
Rydberg constant (R)	$1.0973731534 \times 10^{7}$ m^{-1} = $2.1798736 \times 10^{-18}$ J
speed of light (in vacuum) (c)	2.99792458×10^{8} m s^{-1}

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APPENDIX E: POLYATOMIC IONS

Common Polyatomic Ions

Table E.1 Common Polyatomic Ions

Name	Symbol
Acetate	$C_2H_3O_2^-$
Amide	NH_2^-
Ammonium	NH_4^+
Arsenate	AsO_4^{3-}
Borate	BO_3^{3-}
Bromate	BrO_3^-
Carbonate	CO_3^{2-}
Chlorate	CIO_3^-
Chlorite	CIO_2^-
Chromate	CrO_4^{2-}
Cyanide	CN^-
Dichromate	CrO_7^{2-}
Dihydrogen phosphate	$H_2PO_4^{2-}$
Hydrogen carbonate	HCO_3^-
Hydrogen oxalate	$HC_2O_4^-$
Hydrogen phosphate	HPO_4^{2-}
Hydrogen sulfate (bisulfate)	HSO_4^-
Hydrogen sulfite (bisulfate)	HSO_3^-
Hydroxide	OH^-

Name	**Symbol**
Hypobromite	BrO^-
Hypochlorite	CIO^-
Hypoiodite	IO^-
Iodate	IO_3^-
Nitrate	NO_3^-
Nitrite	NO_2^-
Oxalate	$C_2O_4^{2-}$
Perchlorate	CIO_4^-
Periodate	IO_4^-
Permanganate	MnO_4^-
Peroxide	O_2^{2-}
Phosphate	PO_4^{3-}
Phosphite	PO_3^{3-}
Sulfate	SO_4^{2-}
Sulfite	SO_3^{2-}
Thiocyanide	SCN^-

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APPENDIX F: WATER PROPERTIES

Properties of Water at Various Temperatures

Water Densities

Table F.1 Water Density (kg/m^3) at Different Temperatures (°C)

Temperature[1]	Density
0	999.8395
4	999.9720 (density maximum)
10	999.7026
15	999.1026
20	998.2071
22	997.7735
25	997.0479
30	995.6502
40	992.2
60	983.2
80	971.8
100	958.4

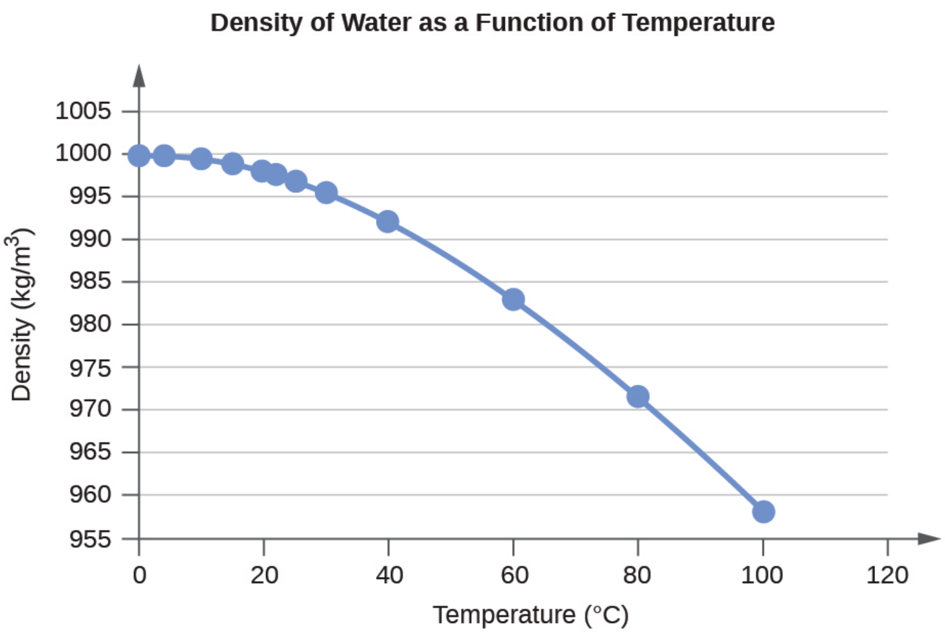

Figure F.1 Density of water (kg/m^3) as a function of Temperature (^{o}C)

Water Vapour Pressures

Table F.2 Water Vapor Pressure (in torr and Pa) at Different Temperatures (°C)

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71
95	633.9	84512.82
100	760.0	101324.7

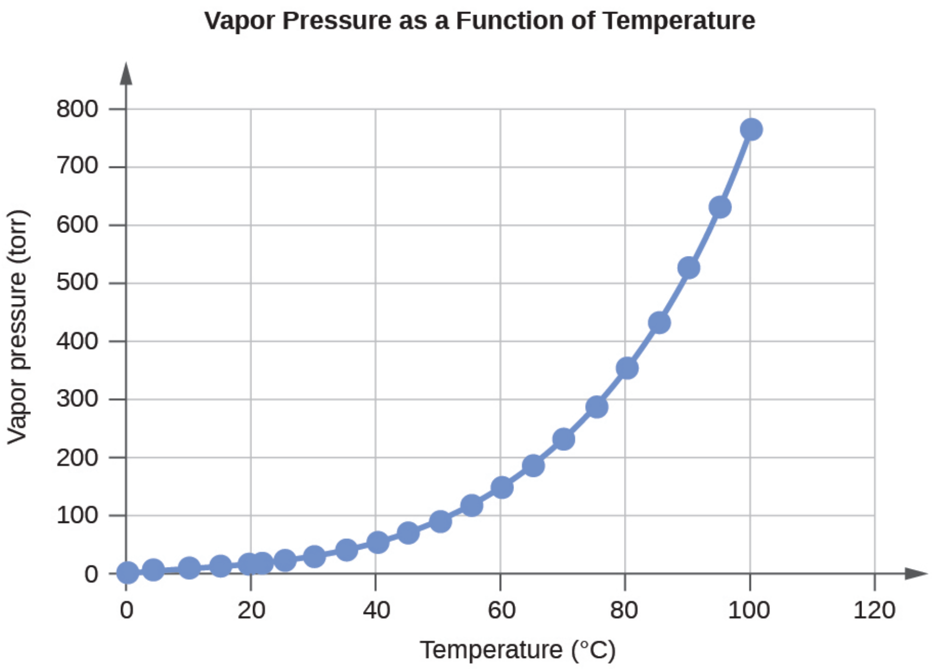

Figure F.2 Vapour pressure (torr) of water as a function of temperature (^{o}C).

Kw of Water

Table F.3 Water K_w and pK_w at Different Temperatures (°C)

Temperature	K_w 10^{-14}	$pK_w{}^2$
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25

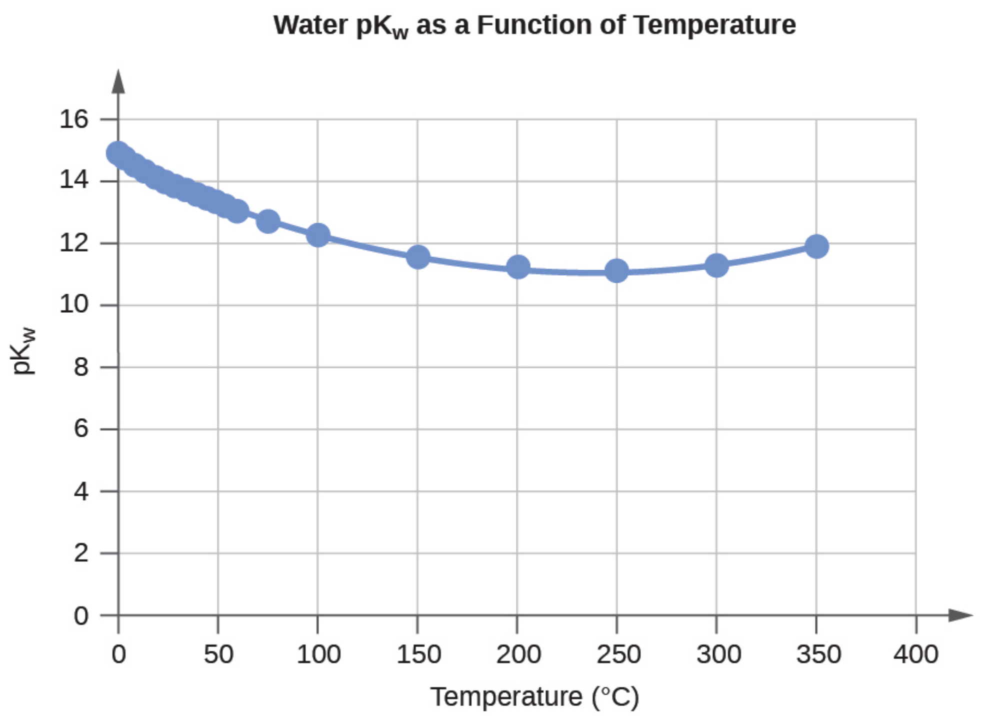

Figure F.3 pKw of water at various temperatures (°C)

Specific Heat Capacity for Water

Specific heat capacity for water (liquid) = 4184 $J{\cdot}K^{-1}{\cdot}kg^{-1}$ = 4.184 $J{\cdot}g^{-1}{\cdot}°C^{-1}$
Specific heat capacity for ice (solid) = 1864 $J{\cdot}K^{-1}{\cdot}kg^{-1}$
Specific heat capacity for steam (gas) = 2093 $J{\cdot}K^{-1}{\cdot}kg^{-1}$

Table F.4 Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

State	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

Cryoscopic constant – K_f = 1.86°C·kg·mol^{-1}
Ebullioscopic constant – K_b = 0.51°C·kg·mol^{-1}

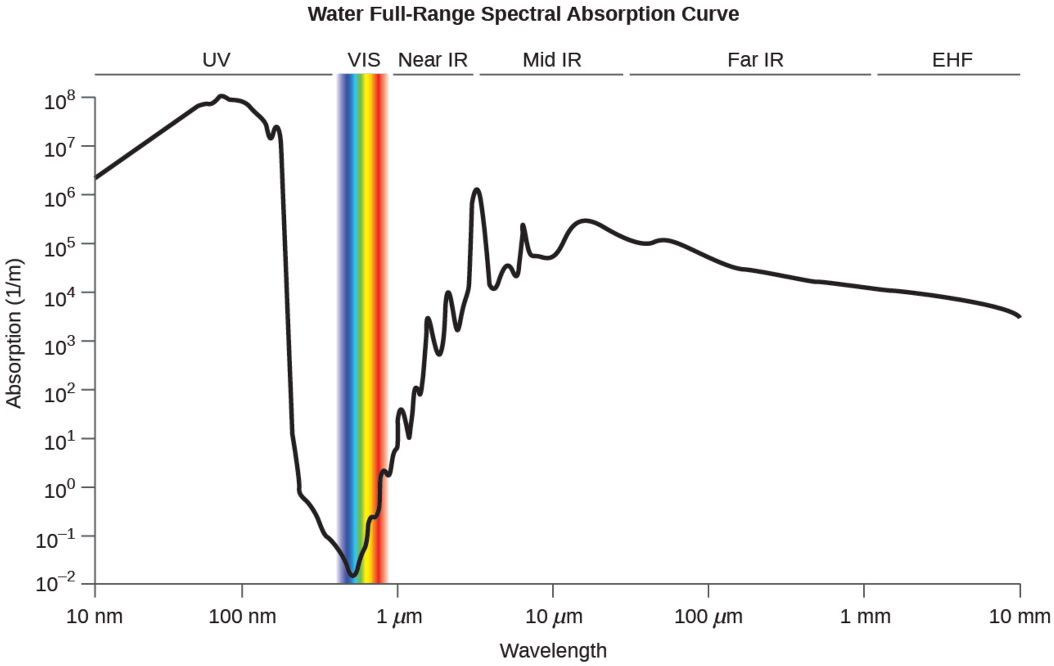

Figure F.4. Water full-range spectral absorption curve. This curve shows the full-range spectral absorption for water. The y-axis signifies the absorption in 1/cm. If we divide 1 by this value, we will obtain the length of the path (in cm) after which the intensity of a light beam passing through water decays by a factor of the base of the natural logarithm e (e = 2.718281828).

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Notes

1. Data for $t < 0$ °C are for supercooled water
2. $pK_w = -\log_{10}(K_w)$

APPENDIX G: COMPOSITION OF COMMERCIAL ACIDS AND BASES

Commercial Acids and Bases

Table G.1 Composition of Commercial Acids and Bases

Acid or Base[1]	Density (g/mL)[2]	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4
aqueous ammonia[3]	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

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Notes

1. Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.
2. This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.
3. This solution is sometimes called "ammonium hydroxide," although this term is not chemically accurate.

APPENDIX H: STANDARD THERMODYNAMIC PROPERTIES FOR SELECTED SUBSTANCES

Thermodynamic Properties

Table H.1 Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f **(kJ mol^{-})**	ΔG°_f **(kJ mol^{-1})**	S°_{298} **(J K^{-1} mol^{-1})**
aluminum			
$\text{Al}(s)$	0	0	28.3
$\text{Al}(g)$	324.4	285.7	164.54
$\text{Al}^{3+}(aq)$	−531	−485	−321.7
$\text{Al}_2\text{O}_3(s)$	−1676	−1582	50.92
$\text{AlF}_3(s)$	−1510.4	−1425	66.5
$\text{AlCl}_3(s)$	−704.2	−628.8	110.67
$\text{AlCl}_3{\cdot}6\text{H}_2\text{O}(s)$	−2691.57	−2269.40	376.56
$\text{Al}_2\text{S}_3(s)$	−724.0	−492.4	116.9
$\text{Al}_2(\text{SO}_4)_3(s)$	−3445.06	−3506.61	239.32
antimony			
$\text{Sb}(s)$	0	0	45.69
$\text{Sb}(g)$	262.34	222.17	180.16
$\text{Sb}_4\text{O}_6(s)$	−1440.55	−1268.17	220.92
$\text{SbCl}_3(g)$	−313.8	−301.2	337.80
$\text{SbCl}_5(g)$	−394.34	−334.29	401.94
$\text{Sb}_2\text{S}_3(\text{s})$	−174.89	−173.64	182.00
$\text{SbCl}_3(\text{s})$	−382.17	−323.72	184.10
$\text{SbOCl}(\text{s})$	−374.0	—	—
arsenic			
$\text{As}(s)$	0	0	35.1
$\text{As}(g)$	302.5	261.0	174.21
$\text{As}_4(g)$	143.9	92.4	314
$\text{As}_4\text{O}_6(s)$	−1313.94	−1152.52	214.22
$\text{As}_2\text{O}_5(s)$	−924.87	−782.41	105.44
$\text{AsCl}_3(g)$	−261.50	−248.95	327.06
$\text{As}_2\text{S}_3(s)$	−169.03	−168.62	163.59
$\text{AsH}_3(g)$	66.44	68.93	222.78
$\text{H}_3\text{AsO}_4(s)$	−906.3	—	—

Substance	ΔH_f° **(kJ mol^{-})**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
barium			
Ba(*s*)	0	0	62.5
Ba(*g*)	180	146	170.24
Ba^{2+}(*aq*)	−537.6	−560.8	9.6
BaO(*s*)	−548.0	−520.3	72.1
$BaCl_2$(*s*)	−855.0	−806.7	123.7
$BaSO_4$(*s*)	−1473.2	−1362.3	132.2
beryllium			
Be(*s*)	0	0	9.50
Be(*g*)	324.3	286.6	136.27
BeO(*s*)	−609.4	−580.1	13.8
bismuth			
Bi(*s*)	0	0	56.74
Bi(*g*)	207.1	168.2	187.00
Bi_2O_3(*s*)	−573.88	−493.7	151.5
$BiCl_3$(*s*)	−379.07	−315.06	176.98
Bi_2S_3(*s*)	−143.1	−140.6	200.4
boron			
B(*s*)	0	0	5.86
B(*g*)	565.0	521.0	153.4
B_2O_3(*s*)	−1273.5	−1194.3	53.97
B_2H_6(*g*)	36.4	87.6	232.1
H_3BO_3(*s*)	−1094.33	−968.92	88.83
BF_3(*g*)	−1136.0	−1119.4	254.4
BCl_3(*g*)	−403.8	−388.7	290.1
$B_3N_3H_6$(*l*)	−540.99	−392.79	199.58
HBO_2(*s*)	−794.25	−723.41	37.66
bromine			
Br_2(*l*)	0	0	152.23
Br_2(*g*)	30.91	3.142	245.5

Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
Br(*g*)	111.88	82.429	175.0
Br^-(*aq*)	–120.9	–102.82	80.71
BrF_3(*g*)	–255.60	–229.45	292.42
HBr(*g*)	–36.3	–53.43	198.7
cadmium			
Cd(*s*)	0	0	51.76
Cd(*g*)	112.01	77.41	167.75
Cd^{2+}(*aq*)	–75.90	–77.61	–73.2
CdO(*s*)	–258.2	–228.4	54.8
$CdCl_2$(*s*)	–391.5	–343.9	115.3
$CdSO_4$(*s*)	–933.3	–822.7	123.0
CdS(*s*)	–161.9	–156.5	64.9
calcium			
Ca(*s*)	0	0	41.6
Ca(*g*)	178.2	144.3	154.88
Ca^{2+}(*aq*)	–542.96	–553.04	–55.2
CaO(*s*)	–634.9	–603.3	38.1
$Ca(OH)_2$(*s*)	–985.2	–897.5	83.4
$CaSO_4$(s)	–1434.5	–1322.0	106.5
$CaSO_4{\cdot}2H_2O$(*s*)	–2022.63	–1797.45	194.14
$CaCO_3$(*s*) (calcite)	–1220.0	–1081.4	110.0
$CaSO_3{\cdot}H_2O$(*s*)	–1752.68	–1555.19	184.10
carbon			
C(*s*) (graphite)	0	0	5.740
C(*s*) (diamond)	1.89	2.90	2.38
C(*g*)	716.681	671.2	158.1
CO(*g*)	–110.52	–137.15	197.7
CO_2(*g*)	–393.51	–394.36	213.8
CO_3^{2-}(*aq*)	–677.1	–527.8	–56.9

Substance	ΔH°_f **(kJ mol^{-})**	ΔG°_f **(kJ mol^{-1})**	S°_{298} **(J K^{-1} mol^{-1})**
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3^-(aq)$	–691.11	–587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
cesium			
$Cs^+(aq)$	–248	–282.0	133

Substance	ΔH_f° **(kJ mol^{-})**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$Cl^-(aq)$	−167.2	−131.2	56.5
$ClF(g)$	−54.48	−55.94	217.78
$ClF_3(g)$	−158.99	−118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	−92.307	−95.299	186.9
$HClO_4(l)$	−40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$CrO_4^{2-}(aq)$	−881.2	−727.8	50.21
$Cr_2O_7^{2-}(aq)$	−1490.3	−1301.1	261.9
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
$CrO_3(s)$	−589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	−1806.7	—	—
cobalt			
$Co(s)$	0	0	30.0
$Co^{2+}(aq)$	−67.4	−51.5	−155
$Co^{3+}(aq)$	92	134	−305.0
$CoO(s)$	−237.9	−214.2	52.97
$Co_3O_4(s)$	−910.02	−794.98	114.22
$Co(NO_3)_2(s)$	−420.5	—	—
copper			
$Cu(s)$	0	0	33.15
$Cu(g)$	338.32	298.58	166.38

Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$Cu^+(aq)$	51.9	50.2	–26
$Cu^{2+}(aq)$	64.77	65.49	–99.6
$CuO(s)$	–157.3	–129.7	42.63
$Cu_2O(s)$	–168.6	–146.0	93.14
$CuS(s)$	–53.1	–53.6	66.5
$Cu_2S(s)$	–79.5	–86.2	120.9
$CuSO_4(s)$	–771.36	–662.2	109.2
$Cu(NO_3)_2(s)$	–302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
$F(g)$	79.4	62.3	158.8
$F^-(aq)$	–332.6	–278.8	–13.8
$F_2O(g)$	24.7	41.9	247.43
$HF(g)$	–273.3	–275.4	173.8
hydrogen			
$H_2(g)$	0	0	130.7
$H(g)$	217.97	203.26	114.7
$H^+(aq)$	0	0	0
$OH^-(aq)$	–230.0	–157.2	–10.75
$H_3O^+(aq)$	–285.8		69.91
$H_2O(l)$	–285.83	–237.1	70.0
$H_2O(g)$	–241.82	–228.59	188.8
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(g)$	–136.3	–105.6	232.7
$HF(g)$	–273.3	–275.4	173.8
$HCl(g)$	–92.307	–95.299	186.9
$HBr(g)$	–36.3	–53.43	198.7
$HI(g)$	26.48	1.70	206.59
$H_2S(g)$	–20.6	–33.4	205.8

Substance	ΔH_f° **(kJ mol^{-})**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$H_2Se(g)$	29.7	15.9	219.0
iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.438	19.3	260.7
$I(g)$	106.84	70.2	180.8
$I^-(aq)$	−55.19	−51.57	11.13
$IF(g)$	95.65	−118.49	236.06
$ICl(g)$	17.78	−5.44	247.44
$IBr(g)$	40.84	3.72	258.66
$IF_7(g)$	−943.91	−818.39	346.44
$HI(g)$	26.48	1.70	206.59
iron			
$Fe(s)$	0	0	27.3
$Fe(g)$	416.3	370.7	180.5
$Fe^{2+}(aq)$	−89.1	−78.90	−137.7
$Fe^{3+}(aq)$	−48.5	−4.7	−315.9
$Fe_2O_3(s)$	−824.2	−742.2	87.40
$Fe_3O_4(s)$	−1118.4	−1015.4	146.4
$Fe(CO)_5(l)$	−774.04	−705.42	338.07
$Fe(CO)_5(g)$	−733.87	−697.26	445.18
$FeCl_2(s)$	−341.79	−302.30	117.95
$FeCl_3(s)$	−399.49	−334.00	142.3
$FeO(s)$	−272.0	−255.2	60.75
$Fe(OH)_2(s)$	−569.0	−486.5	88.
$Fe(OH)_3(s)$	−823.0	−696.5	106.7
$FeS(s)$	−100.0	−100.4	60.29
$Fe_3C(s)$	25.10	20.08	104.60
lead			
$Pb(s)$	0	0	64.81
$Pb(g)$	195.2	162.	175.4

Substance	ΔH°_f **(kJ mol^{-})**	ΔG°_f **(kJ mol^{-1})**	S°_{298} **(J K^{-1} mol^{-1})**
$Pb^{2+}(aq)$	−1.7	−24.43	10.5
$PbO(s)$ (yellow)	−217.32	−187.89	68.70
$PbO(s)$ (red)	−218.99	−188.93	66.5
$Pb(OH)_2(s)$	−515.9	—	—
$PbS(s)$	−100.4	−98.7	91.2
$Pb(NO_3)_2(s)$	−451.9	—	—
$PbO_2(s)$	−277.4	−217.3	68.6
$PbCl_2(s)$	−359.4	−314.1	136.0
lithium			
$Li(s)$	0	0	29.1
$Li(g)$	159.3	126.6	138.8
$Li^{+}(aq)$	−278.5	−293.3	13.4
$LiH(s)$	−90.5	−68.3	20.0
$Li(OH)(s)$	−487.5	−441.5	42.8
$LiF(s)$	−616.0	−587.5	35.7
$Li_2CO_3(s)$	−1216.04	−1132.19	90.17
magnesium			
$Mg^{2+}(aq)$	−466.9	−454.8	−138.1
manganese			
$Mn(s)$	0	0	32.0
$Mn(g)$	280.7	238.5	173.7
$Mn^{2+}(aq)$	−220.8	−228.1	−73.6
$MnO(s)$	−385.2	−362.9	59.71
$MnO_2(s)$	−520.03	−465.1	53.05
$Mn_2O_3(s)$	−958.97	−881.15	110.46
$Mn_3O_4(s)$	−1378.83	−1283.23	155.64
$MnO_4^{-}(aq)$	−541.4	−447.2	191.2
$MnO_4^{2-}(aq)$	−653.0	−500.7	59
mercury			

Substance	$\Delta H_\mathrm{f}^\circ$ **(kJ mol^{-})**	$\Delta G_\mathrm{f}^\circ$ **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
Hg(*l*)	0	0	75.9
Hg(*g*)	61.4	31.8	175.0
$Hg^{2+}(aq)$		164.8	
$Hg^{2+}(aq)$	172.4	153.9	84.5
HgO(*s*) (red)	−90.83	−58.5	70.29
HgO(*s*) (yellow)	−90.46	−58.43	71.13
$HgCl_2(s)$	−224.3	−178.6	146.0
$Hg_2Cl_2(s)$	−265.4	−210.7	191.6
HgS(*s*) (red)	−58.16	−50.6	82.4
HgS(*s*) (black)	−53.56	−47.70	88.28
$HgSO_4(s)$	−707.51	−594.13	0.00
nickel			
$Ni^{2+}(aq)$	−64.0	−46.4	−159
nitrogen			
$N_2(g)$	0	0	191.6
N(*g*)	472.704	455.5	153.3
NO(*g*)	90.25	87.6	210.8
$NO_2(g)$	33.2	51.30	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_3(g)$	83.72	139.41	312.17
$NO_3^-(aq)$	−205.0	−108.7	146.4
$N_2O_4(g)$	11.1	99.8	304.4
$N_2O_5(g)$	11.3	115.1	355.7
$NH_3(g)$	−45.9	−16.5	192.8
$NH_4^+(aq)$	−132.5	−79.31	113.4
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	−365.56	−183.87	151.08
$NH_4Cl(s)$	−314.43	−202.87	94.6

Substance	$\Delta H_\mathrm{f}^\circ$ **(kJ mol^{-})**	$\Delta G_\mathrm{f}^\circ$ **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
$O(g)$	249.17	231.7	161.1
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$PO_4{}^{3-}(aq)$	–1277	–1019	–222
$HPO_3(s)$	–948.5	—	—
$HPO_4{}^{2-}(aq)$	–1292.1	–1089.3	–33
$H_2PO_4{}^{2-}(aq)$	–1296.3	–1130.4	90.4
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			

Substance	ΔH_f° **(kJ mol^{-})**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
K(*s*)	0	0	64.7
K(*g*)	89.0	60.5	160.3
K^+(*aq*)	–252.4	–283.3	102.5
KF(*s*)	–576.27	–537.75	66.57
KCl(*s*)	–436.5	–408.5	82.6
rubidium			
Rb^+(*aq*)	–246	–282.2	124
silicon			
Si(*s*)	0	0	18.8
Si(*g*)	450.0	405.5	168.0
SiO_2(*s*)	–910.7	–856.3	41.5
SiH_4(*g*)	34.3	56.9	204.6
H_2SiO_3(*s*)	–1188.67	–1092.44	133.89
H_4SiO_4(*s*)	–1481.14	–1333.02	192.46
SiF_4(*g*)	–1615.0	–1572.8	282.8
$SiCl_4$(*l*)	–687.0	–619.8	239.7
$SiCl_4$(*g*)	–662.75	–622.58	330.62
SiC(*s, beta cubic*)	–73.22	–70.71	16.61
SiC(*s, alpha hexagonal*)	–71.55	–69.04	16.48
silver			
Ag(*s*)	0	0	42.55
Ag(*g*)	284.9	246.0	172.89
Ag^+(*aq*)	105.6	77.11	72.68
Ag_2O(*s*)	–31.05	–11.20	121.3
AgCl(*s*)	–127.0	–109.8	96.3
Ag_2S(*s*)	–32.6	–40.7	144.0
sodium			
Na(*s*)	0	0	51.3
Na(*g*)	107.5	77.0	153.7

Substance	ΔH_f° **(kJ mol^{-})**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$Na^+(aq)$	−240.1	−261.9	59
$Na_2O(s)$	−414.2	−375.5	75.1
$NaCl(s)$	−411.2	−384.1	72.1
strontium			
$Sr^{2+}(aq)$	−545.8	−557.3	−32.6
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
$S(g)$	278.81	238.25	167.82
$S^{2-}(aq)$	41.8	83.7	22
$SO_2(g)$	−296.83	−300.1	248.2
$SO_3(g)$	−395.72	−371.06	256.76
$SO_4{}^{2-}(aq)$	−909.3	−744.5	20.1
$S_2O_3{}^{2-}(aq)$	−648.5	−522.5	67
$H_2S(g)$	−20.6	−33.4	205.8
$HS^-(aq)$	−17.7	12.6	61.1
$H_2SO_4(l)$	−813.989	690.00	156.90
$HSO_4{}^{2-}(aq)$	−885.75	−752.87	126.9
$H_2S_2O_7(s)$	−1273.6	—	—
$SF_4(g)$	−728.43	−684.84	291.12
$SF_6(g)$	−1220.5	−1116.5	291.5
$SCl_2(l)$	−50	—	—
$SCl_2(g)$	−19.7	—	—
$S_2Cl_2(l)$	−59.4	—	—
$S_2Cl_2(g)$	−19.50	−29.25	319.45
$SOCl_2(g)$	−212.55	−198.32	309.66
$SOCl_2(l)$	−245.6	—	—
$SO_2Cl_2(l)$	−394.1	—	—
$SO_2Cl_2(g)$	−354.80	−310.45	311.83
tin			

Substance	$\Delta H_\mathrm{f}^\circ$ **(kJ mol^{-})**	$\Delta G_\mathrm{f}^\circ$ **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
Sn(*s*)	0	0	51.2
Sn(*g*)	301.2	266.2	168.5
SnO(*s*)	–285.8	–256.9	56.5
SnO_2(*s*)	–577.6	–515.8	49.0
$SnCl_4$(*l*)	–511.3	–440.1	258.6
$SnCl_4$(*g*)	–471.5	–432.2	365.8
titanium			
Ti(*s*)	0	0	30.7
Ti(*g*)	473.0	428.4	180.3
TiO_2(*s*)	–944.0	–888.8	50.6
$TiCl_4$(*l*)	–804.2	–737.2	252.4
$TiCl_4$(*g*)	–763.2	–726.3	353.2
tungsten			
W(*s*)	0	0	32.6
W(*g*)	849.4	807.1	174.0
WO_3(*s*)	–842.9	–764.0	75.9
zinc			
Zn(*s*)	0	0	41.6
Zn(*g*)	130.73	95.14	160.98
Zn^{2+}(*aq*)	–153.9	–147.1	–112.1
ZnO(*s*)	–350.5	–320.5	43.7
$ZnCl_2$(*s*)	–415.1	–369.43	111.5
ZnS(*s*)	–206.0	–201.3	57.7
$ZnSO_4$(*s*)	–982.8	–871.5	110.5
$ZnCO_3$(*s*)	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—

Substance	$\Delta H_\mathrm{f}^\circ$ **(kJ mol^{-})**	$\Delta G_\mathrm{f}^\circ$ **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$[Co(NH_3)_4Cl_2]Cl$, *cis*	−874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	−877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	−689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	−681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	−677.4	—	—
$[Co(en)_3](ClO_4)_3$	−762.7	—	—
$[Co(en)_3]Br_2$	−595.8	—	—
$[Co(en)_3]I_2$	−475.3	—	—
$[Co(en)_3]I_3$	−519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	−1034.7	−221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	−1088.7	−412.9	331
$[Co(NH_3)_6](NO_3)_3$	−1282.0	−524.5	448
$[Co(NH_3)_5Cl]Cl_2$	−1017.1	−582.5	366.1
$[Pt(NH_3)_4]Cl_2$	−725.5	—	—
$[Ni(NH_3)_6]Cl_2$	−994.1	—	—
$[Ni(NH_3)_6]Br_2$	−923.8	—	—
$[Ni(NH_3)_6]I_2$	−808.3	—	—

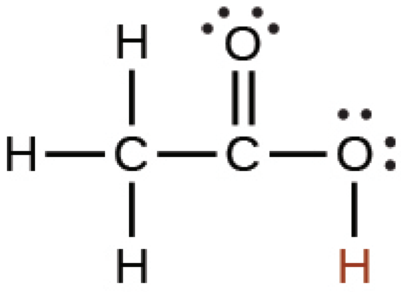
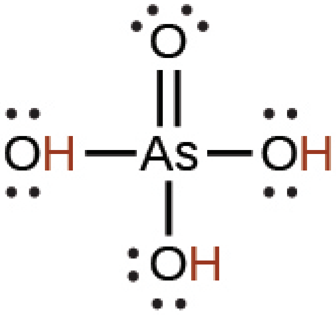
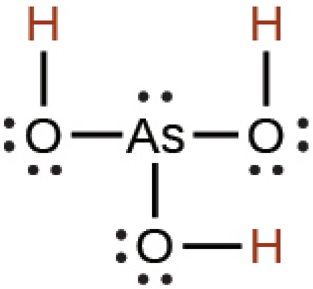
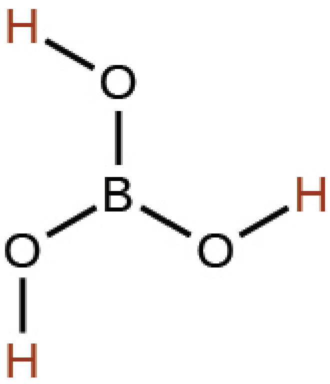
Attribution & References

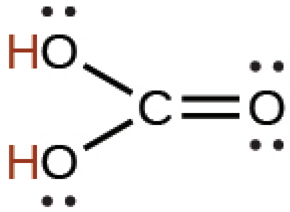
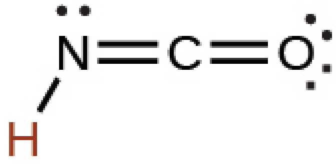
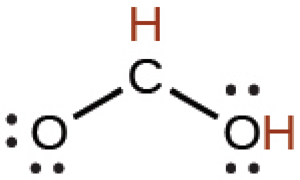
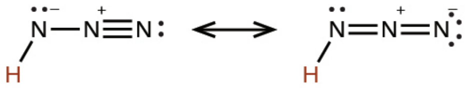
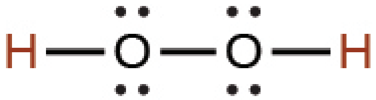
Except where otherwise noted, this page is adapted from "Appendix G: Standard Thermodynamic Properties for Selected Substances" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)*

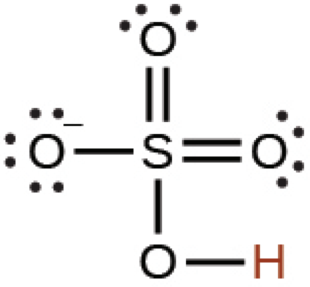
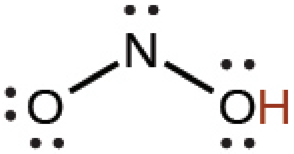
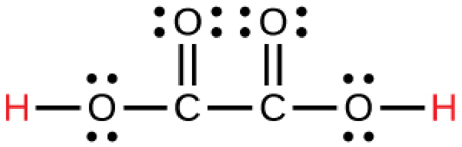
APPENDIX I: IONIZATION CONSTANTS OF WEAK ACIDS

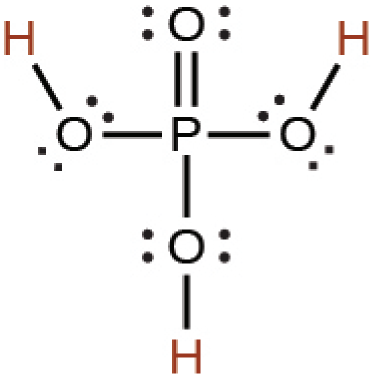
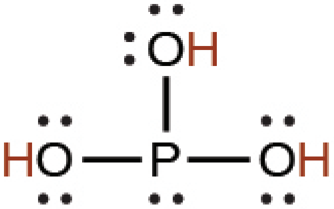
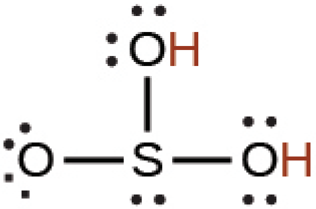
Ionization Constants of Weak Acids

Table I.1 Ionization Constants of Weak Acids

Acid	**Formula**	**K_a at 25 °C**	**Lewis Structure**
acetic	$CH_3CO_2\mathbf{H}$	1.8×10^{-5}	
arsenic	$\mathbf{H_3}AsO_4$	5.5×10^{-3}	
	$H_2AsO_4{}^{-}$	1.7×10^{-7}	
	$HAsO_4{}^{2-}$	5.1×10^{-12}	
arsenous	$\mathbf{H_3}AsO_3$	5.1×10^{-10}	
boric	$\mathbf{H_3}BO_3$	5.4×10^{-10}	

Acid	**Formula**	**K_a at 25 °C**	**Lewis Structure**
carbonic	$\mathbf{H}_2\mathrm{CO}_3$	4.3×10^{-7}	
	HCO_3^-	5.6×10^{-11}	
cyanic	$\mathbf{H}\mathrm{CNO}$	2×10^{-4}	
formic	$\mathrm{HCO}_2\mathbf{H}$	1.8×10^{-4}	
hydrazoic	$\mathbf{H}\mathrm{N}_3$	2.5×10^{-5}	
hydrocyanic	$\mathbf{H}\mathrm{CN}$	4.9×10^{-10}	
hydrofluoric	$\mathbf{H}\mathrm{F}$	3.5×10^{-4}	
hydrogen peroxide	$\mathbf{H}_2\mathrm{O}_2$	2.4×10^{-12}	
hydrogen selenide	$\mathbf{H}_2\mathrm{Se}$	1.29×10^{-4}	
	$\mathbf{H}\mathrm{Se}^-$	1×10^{-12}	

Acid	**Formula**	**K_a at 25 °C**	**Lewis Structure**
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	
	HTe^-	1.6×10^{-11}	
hypobromous	$HBrO$	2.8×10^{-9}	
hypochlorous	$HClO$	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	
oxalic	$H_2C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^-$	6.1×10^{-5}	

Acid	Formula	K_a at 25 °C	Lewis Structure
phosphoric	H_3PO_4	7.5×10^{-3}	
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

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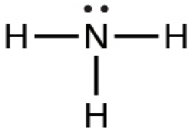
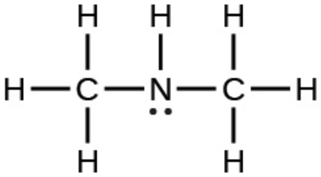
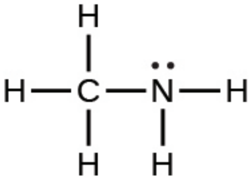
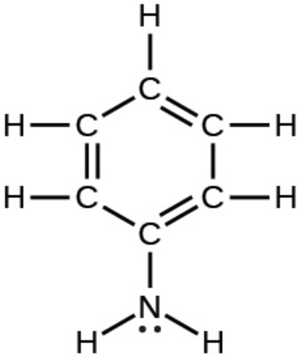
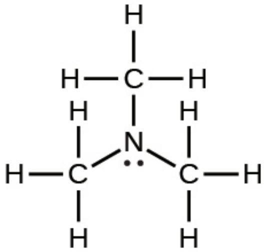
APPENDIX J: IONIZATION CONSTANTS OF WEAK BASES

Ionization Constants of Weak Bases

Table J.1 Ionization Constants of Weak Bases

Base	Lewis Structure	K_b at 25 °C
ammonia		1.8×10^{-5}
dimethylamine		5.9×10^{-4}
methylamine		4.4×10^{-4}
phenylamine (aniline)		4.3×10^{-10}
trimethylamine		6.3×10^{-5}

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APPENDIX K: SOLUBILITY PRODUCTS

Solubility Products

Table K.1 Solubility Products

Main Element	**Substance**	K_{sp} **at 25 °C**
aluminum	$Al(OH)_3$	2×10^{-32}
barium	$BaCO_3$	1.6×10^{-9}
barium	$BaC_2O_4{\cdot}2H_2O$	1.1×10^{-7}
barium	$BaSO_4$	2.3×10^{-8}
barium	$BaCrO_4$	8.5×10^{-11}
barium	BaF_2	2.4×10^{-5}
barium	$Ba(OH)_2{\cdot}8H_2O$	5.0×10^{-3}
barium	$Ba_3(PO_4)_2$	6×10^{-39}
barium	$Ba_3(AsO_4)_2$	1.1×10^{-13}
bismuth	$BiO(OH)$	4×10^{-10}
bismuth	$BiOCl$	1.8×10^{-31}
bismuth	Bi_2S_3	1×10^{-97}
cadmium	$Cd(OH)_2$	5.9×10^{-15}
cadmium	CdS	1.0×10^{-28}
cadmium	$CdCO_3$	5.2×10^{-12}
calcium	$Ca(OH)_2$	1.3×10^{-6}
calcium	$CaCO_3$	8.7×10^{-9}
calcium	$CaSO4{\cdot}2H_2O$	6.1×10^{-5}
calcium	$CaC_2O_4{\cdot}H_2O$	1.96×10^{-8}
calcium	$Ca_3(PO_4)_2$	1.3×10^{-32}
calcium	$CaHPO_4$	7×10^{-7}
calcium	CaF_2	4.0×10^{-11}
chromium	$Cr(OH)_3$	6.7×10^{-31}
cobalt	$Co(OH)_2$	2.5×10^{-16}
cobalt	$CoS(\alpha)$	5×10^{-22}
cobalt	$CoS(\beta)$	3×10^{-26}
cobalt	$CoCO_3$	1.4×10^{-13}

Main Element	**Substance**	**K_{sp} at 25 °C**
cobalt	$Co(OH)_3$	2.5×10^{-43}
copper	CuCl	1.2×10^{-6}
copper	CuBr	6.27×10^{-9}
copper	CuI	1.27×10^{-12}
copper	CuSCN	1.6×10^{-11}
copper	Cu_2S	2.5×10^{-48}
copper	$Cu(OH)_2$	2.2×10^{-20}
copper	CuS	8.5×10^{-45}
copper	$CuCO_3$	2.5×10^{-10}
iron	$Fe(OH)_2$	1.8×10^{-15}
iron	$FeCO_3$	2.1×10^{-11}
iron	FeS	3.7×10^{-19}
iron	$Fe(OH)_3$	4×10^{-38}
lead	$Pb(OH)_2$	1.2×10^{-15}
lead	PbF_2	4×10^{-8}
lead	$PbCl_2$	1.6×10^{-5}
lead	$PbBr_2$	4.6×10^{-6}
lead	PbI_2	1.4×10^{-8}
lead	$PbCO_3$	1.5×10^{-15}
lead	PbS	7×10^{-29}
lead	$PbCrO_4$	2×10^{-16}
lead	$PbSO_4$	1.3×10^{-8}
lead	$Pb_3(PO_4)_2$	1×10^{-54}
magnesium	$Mg(OH)_2$	8.9×10^{-12}
magnesium	$MgCO_3 \cdot 3H_2O$	*ca* 1×10^{-5}
magnesium	$MgNH_4PO_4$	3×10^{-13}
magnesium	MgF_2	6.4×10^{-9}
magnesium	MgC_2O_4	7×10^{-7}

Main Element	Substance	K_{sp} at 25 °C
manganese	$Mn(OH)_2$	2×10^{-13}
manganese	$MnCO_3$	8.8×10^{-11}
manganese	MnS	2.3×10^{-13}
mercury	$Hg_2O{\cdot}H_2O$	3.6×10^{-26}
mercury	Hg_2Cl_2	1.1×10^{-18}
mercury	Hg_2Br_2	1.3×10^{-22}
mercury	Hg_2I_2	4.5×10^{-29}
mercury	Hg_2CO_3	9×10^{-15}
mercury	Hg_2SO_4	7.4×10^{-7}
mercury	Hg_2S	1.0×10^{-47}
mercury	Hg_2CrO_4	2×10^{-9}
mercury	HgS	1.6×10^{-54}
nickel	$Ni(OH)_2$	1.6×10^{-16}
nickel	$NiCO_3$	1.4×10^{-7}
nickel	$NiS(\alpha)$	4×10^{-20}
nickel	$NiS(\beta)$	1.3×10^{-25}
potassium	$KClO_4$	1.05×10^{-2}
potassium	K_2PtCl_6	7.48×10^{-6}
potassium	$KHC_4H_4O_6$	3×10^{-4}
silver	$\frac{1}{2}Ag_2O(Ag^+ + OH^-)$	2×10^{-8}
silver	$AgCl$	1.6×10^{-10}
silver	$AgBr$	5.0×10^{-13}
silver	AgI	1.5×10^{-16}
silver	$AgCN$	1.2×10^{-16}
silver	$AgSCN$	1.0×10^{-12}
silver	Ag_2S	1.6×10^{-49}
silver	Ag_2CO_3	8.1×10^{-12}
silver	Ag_2CrO_4	9.0×10^{-12}

Main Element	**Substance**	**K_{sp} at 25 °C**
silver	$Ag_4Fe(CN)_6$	1.55×10^{-41}
silver	Ag_2SO_4	1.2×10^{-5}
silver	Ag_3PO_4	1.8×10^{-18}
strontium	$Sr(OH)_2{\cdot}8H_2O$	3.2×10^{-4}
strontium	$SrCO_3$	7×10^{-10}
strontium	$SrCrO_4$	3.6×10^{-5}
strontium	$SrSO_4$	3.2×10^{-7}
strontium	$SrC_2O_4{\cdot}H_2O$	4×10^{-7}
thallium	TlCl	1.7×10^{-4}
thallium	TlSCN	1.6×10^{-4}
thallium	Tl_2S	6×10^{-22}
thallium	$Tl(OH)_3$	6.3×10^{-46}
tin	$Sn(OH)_2$	3×10^{-27}
tin	SnS	1×10^{-26}
tin	$Sn(OH)_4$	1.0×10^{-57}
zinc	$ZnCO_3$	2×10^{-10}

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APPENDIX L: FORMATION CONSTANTS FOR COMPLEX IONS

Formation Constants – Complex Ions

Table L.1 Formation Constants for Complex Ions

Equilibrium	K_f
$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	7 × 10^{19}
$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3 × 10^7
$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	3 × 10^{18}
$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3 × 10^5
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	2.3 × 10^{33}
$Cu^{+} + 2CN \rightleftharpoons [Cu(CN)_2]^{-}$	1.0 × 10^{16}
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.7 × 10^{13}
$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.5 × 10^{35}
$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	2 × 10^{43}
$Fe^{3+} + 6SCN^- \rightleftharpoons [Fe(SCN)_6]^{3-}$	3.2 × 10^3
$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.1 × 10^{16}
$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	2.0 × 10^8
$Ag^{+} + 2Cl^- \rightleftharpoons [AgCl_2]^{-}$	1.8 × 10^5
$Ag^{+} + 2CN^- \rightleftharpoons [Ag(CN)_2]^{-}$	1 × 10^{21}
$Ag^{+} + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^{+}$	1.7 × 10^7
$Zn^{2+} + 4CN^- \rightleftharpoons [Zn(CN)_4]^{2-}$	2.1 × 10^{19}
$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	2 × 10^{15}
$Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$	8.9 × 10^2
$Ag^{+} + 4SCN^- \rightleftharpoons [Ag(SCN)_4]^{3-}$	1.2 × 10^{10}
$Pb^{2+} + 4I^- \rightleftharpoons [PbI_4]^{2-}$	3.0 × 10^4
$Pt^{2+} + 4Cl^- \rightleftharpoons [PtCl_4]^{2-}$	1 × 10^{16}
$Cu^{2+} + 4CN \rightleftharpoons [Cu(CN)_4]^{2-}$	1.0 × 10^{25}

Equilibrium	K_f
$Co^{2+} + 4SCN^- \rightleftharpoons [Co(SCN)_4]^{2-}$	1×10^3

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APPENDIX M: STANDARD ELECTRODE (HALF-CELL) POTENTIALS

Standard Electrode Potentials

Table M.1 Standard Electrode (Half-Cell) Potentials

Half-Reaction	***E*° (V)**
$\mathrm{Ag^{+} + e^{-} \longrightarrow Ag}$	+0.7996
$\mathrm{AgCl + e^{-} \longrightarrow Ag + Cl^{-}}$	+0.22233
$\mathrm{[Ag(CN)_2]^{-} + e^{-} \longrightarrow Ag + 2CN^{-}}$	−0.31
$\mathrm{Ag_2CrO_4 + 2e^{-} \longrightarrow 2Ag + CrO_4{}^{2-}}$	+0.45
$\mathrm{[Ag(NH_3)_2]^{+} + e^{-} \longrightarrow Ag + 2NH_3}$	+0.373
$\mathrm{[Ag(S_2O_3)_2]^{3+} + e^{-} \longrightarrow Ag + 2S_2O_3{}^{2-}}$	+0.017
$\mathrm{[AlF_6]^{3-} + 3e^{-} \longrightarrow Al + 6F^{-}}$	−2.07
$\mathrm{Al^{3+} + 3e^{-} \longrightarrow Al}$	−1.662
$\mathrm{Am^{3+} + 3e^{-} \longrightarrow Am}$	−2.048
$\mathrm{Au^{3+} + 3e^{-} \longrightarrow Au}$	+1.498
$\mathrm{Au^{+} + e^{-} \longrightarrow Au}$	+1.692
$\mathrm{Ba^{2+} + 2e^{-} \longrightarrow Ba}$	−2.912
$\mathrm{Be^{2+} + 2e^{-} \longrightarrow Be}$	−1.847
$\mathrm{Br_2}(aq) + \mathrm{2e^{-} \longrightarrow 2Br^{-}}$	+1.0873
$\mathrm{Ca^{2+} + 2e^{-} \longrightarrow Ca}$	−2.868
$\mathrm{Ce^{3} + 3e^{-} \longrightarrow Ce}$	−2.483
$\mathrm{Ce^{4+} + e^{-} \longrightarrow Ce^{3+}}$	+1.61
$\mathrm{Cd^{2+} + 2e^{-} \longrightarrow Cd}$	−0.4030
$\mathrm{[Cd(CN)_4]^{2-} + 2e^{-} \longrightarrow Cd + 4CN^{-}}$	−1.09
$\mathrm{[Cd(NH_3)_4]^{2+} + 2e^{-} \longrightarrow Cd + 4NH_3}$	−0.61
$\mathrm{CdS + 2e^{-} \longrightarrow Cd + S^{2-}}$	−1.17
$\mathrm{Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}}$	+1.35827
$\mathrm{ClO_4{}^{-} + H_2O + 2e^{-} \longrightarrow ClO_3{}^{-} + 2OH^{-}}$	+0.36

$ClO_3{}^- + H_2O + 2e^- \longrightarrow ClO_2{}^- + 2OH^-$	+0.33
$ClO_2{}^- + H_2O + 2e^- \longrightarrow ClO^- + 2OH^-$	+0.66
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89
$ClO_4{}^- + 2H_3O^+ + 2e^- \longrightarrow ClO_3{}^- + 3H_2O$	+1.189
$ClO_3{}^- + 3H_3O^+ + 2e^- \longrightarrow HClO_2 + 4H_2O$	+1.21
$HClO + H_3O^+ + 2e^- \longrightarrow Cl^- + 2H_2O$	+1.482
$HClO + H_3O^+ + e^- \longrightarrow \frac{1}{2}Cl_2 + 2H_2O$	+1.611
$HClO_2 + 2H_3O^+ + 2e^- \longrightarrow HClO + 3H_2O$	+1.628
$Co^{3+} + e^- \longrightarrow Co^{2+}$ (2mol\;//\;H_2SO_4)	+1.83
$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$[Co(NH_3)_6]^{3+} + e^- \longrightarrow [Co(NH_3)_6]^{2+}$	+0.1
$Co(OH)_3 + e^- \longrightarrow Co(OH)_2 + OH^-$	+0.17
$Cr^3 + 3e^- \longrightarrow Cr$	−0.744
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.407
$Cr^{2+} + 2e^- \longrightarrow Cr$	−0.913
$[Cu(CN)_2]^- + e^- \longrightarrow Cu + 2CN^-$	−0.43
$CrO_4{}^{2-} + 4H_2O + 3e^- \longrightarrow Cr(OH)_3 + 5OH^-$	−0.13
$Cr_2O_7{}^{2-} + 14H_3O^+ + 6e^- \longrightarrow 2Cr^{3+} + 21H_2O$	+1.232
$[Cr(OH)_4]^- + 3e^- \longrightarrow Cr + 4OH^-$	−1.2
$Cr(OH)_3 + 3e^- \longrightarrow Cr + 3OH^-$	−1.48
$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.153
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Cu^+ + e^- \longrightarrow Cu$	+0.521
$F_2 + 2e^- \longrightarrow 2F^-$	+2.866

$Fe^{2+} + 2e^{-} \longrightarrow Fe$	−0.447
$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$	+0.771
$[Fe(CN)_6]^{3-} + e^{-} \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_2 + 2e^{-} \longrightarrow Fe + 2OH^{-}$	−0.88
$FeS + 2e^{-} \longrightarrow Fe + S^{2-}$	−1.01
$Ga^{3+} + 3e^{-} \longrightarrow Ga$	−0.549
$Gd^{3+} + 3e^{-} \longrightarrow Gd$	−2.279
$\frac{1}{2}H_2 + e^{-} \longrightarrow H^{-}$	−2.23
$2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-}$	−0.8277
$H_2O_2 + 2H_3O^{+} + 2e^{-} \longrightarrow 4H_2O$	+1.776
$2H_3O^{+} + 2e^{-} \longrightarrow H_2 + 2H_2O$	0.00
$HO_2{}^{-} + H_2O + 2e^{-} \longrightarrow 3OH^{-}$	+0.878
$Hf^{4+} + 4e^{-} \longrightarrow Hf$	−1.55
$Hg^{2+} + 2e^{-} \longrightarrow Hg$	+0.851
$2Hg^{2+} + 2e^{-} \longrightarrow Hg_2{}^{2+}$	+0.92
$Hg_2{}^{2+} + 2e^{-} \longrightarrow 2Hg$	+0.7973
$[HgBr_4]^{2-} + 2e^{-} \longrightarrow Hg + 4Br^{-}$	+0.21
$Hg_2Cl_2 + 2e^{-} \longrightarrow 2Hg + 2Cl^{-}$	+0.26808
$[Hg(CN)_4]^{2-} + 2e^{-} \longrightarrow Hg + 4CN^{-}$	−0.37
$[HgI_4]^{2-} + 2e^{-} \longrightarrow Hg + 4I^{-}$	−0.04
$HgS + 2e^{-} \longrightarrow Hg + S^{2-}$	−0.70
$I_2 + 2e^{-} \longrightarrow 2I^{-}$	+0.5355
$In^{3+} + 3e^{-} \longrightarrow In$	−0.3382
$K^{+} + e^{-} \longrightarrow K$	−2.931

$La^{3+} + 3e^- \longrightarrow La$	−2.52
$Li^{+} + e^- \longrightarrow Li$	−3.04
$Lu^{3+} + 3e^- \longrightarrow Lu$	−2.28
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.185
$MnO_2 + 2H_2O + 2e^- \longrightarrow Mn(OH)_2 + 2OH^-$	−0.05
$MnO_4{}^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.558
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23
$MnO_4{}^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.507
$Na^{+} + e^- \longrightarrow Na$	−2.71
$Nd^{3+} + 3e^- \longrightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.257
$[Ni(NH_3)_6]^{2+} + 2e^- \longrightarrow Ni + 6NH_3$	−0.49
$NiO_2 + 4H^+ + 2e^- \longrightarrow Ni^{2+} + 2H_2O$	+1.593
$NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$	+0.49
$NiS + 2e^- \longrightarrow Ni + S^{2-}$	+0.76
$NO_3{}^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.957
$NO_3{}^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$	+0.92
$NO_3{}^- + H_2O + 2e^- \longrightarrow NO_2{}^- + 2OH^-$	+0.10
$Np^{3+} + 3e^- \longrightarrow Np$	−1.856
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.401
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	+0.695
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.1262
$PbO_2 + SO_4{}^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.69

$PbS + 2e^- \longrightarrow Pb + S^{2-}$	−0.95
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4{}^{2-}$	−0.3505
$Pd^{2+} + 2e^- \longrightarrow Pd$	+0.987
$[PdCl_4]^{2-} + 2e^- \longrightarrow Pd + 4Cl^-$	+0.591
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20
$[PtBr_4]^{2-} + 2e^- \longrightarrow Pt + 4Br^-$	+0.58
$[PtCl_4]^{2-} + 2e^- \longrightarrow Pt + 4Cl^-$	+0.755
$[PtCl_6]^{2-} + 2e^- \longrightarrow [PtCl_4]^{2-} + 2Cl^-$	+0.68
$Pu^3 + 3e^- \longrightarrow Pu$	−2.03
$Ra^{2+} + 2e^- \longrightarrow Ra$	−2.92
$Rb^+ + e^- \longrightarrow Rb$	−2.98
$[RhCl_6]^{3-} + 3e^- \longrightarrow Rh + 6Cl^-$	+0.44
$S + 2e^- \longrightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \longrightarrow H_2S$	+0.142
$Sc^{3+} + 3e^- \longrightarrow Sc$	−2.09
$Se + 2H^+ + 2e^- \longrightarrow H_2Se$	−0.399
$[SiF_6]^{2-} + 4e^- \longrightarrow Si + 6F^-$	−1.2
$SiO_3{}^{2-} + 3H_2O + 4e^- \longrightarrow Si + 6OH^-$	−1.697
$SiO_2 + 4H^+ + 4e^- \longrightarrow Si + 2H_2O$	−0.86
$Sm^{3+} + 3e^- \longrightarrow Sm$	−2.304
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.151
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.1375
$[SnF_6]^{2-} + 4e^- \longrightarrow Sn + 6F^-$	−0.25
$SnS + 2e^- \longrightarrow Sn + S^{2-}$	−0.94

$Sr^{2+} + 2e^{-} \longrightarrow Sr$	−2.89
$TeO_2 + 4H^{+} + 4e^{-} \longrightarrow Te + 2H_2O$	+0.593
$Th^{4+} + 4e^{-} \longrightarrow Th$	−1.90
$Ti^{2+} + 2e^{-} \longrightarrow Ti$	−1.630
$U^{3+} + 3e^{-} \longrightarrow U$	−1.79
$V^{2+} + 2e^{-} \longrightarrow V$	−1.19
$Y^{3+} + 3e^{-} \longrightarrow Y$	−2.37
$Zn^{2+} + 2e^{-} \longrightarrow Zn$	−0.7618
$[Zn(CN)_4]^{2-} + 2e^{-} \longrightarrow Zn + 4CN^{-}$	−1.26
$[Zn(NH_3)_4]^{2+} + 2e^{-} \longrightarrow Zn + 4NH_3$	−1.04
$Zn(OH)_2 + 2e^{-} \longrightarrow Zn + 2OH^{-}$	−1.245
$[Zn(OH)_4]^{2} + 2e^{-} \longrightarrow Zn + 4OH^{-}$	−1.199
$ZnS + 2e^{-} \longrightarrow Zn + S^{2-}$	−1.40
$Zr^{4} + 4e^{-} \longrightarrow Zr$	−1.539

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GLOSSARY

Absolute zero

temperature at which the volume of a gas would be zero according to Charles's law.

Accuracy

How closely a measurement aligns with a correct value

Acid

substance that produces $H3O+$ when dissolved in water

acid dissociation constant, (Ka)

is an equilibrium constant that gives numerical representation of an acid's strength in a solution based its degree of dissociation in water. The greater the Ka, the stronger the acid.

Acid-base reaction

reaction involving the transfer of a hydrogen ion between reactant species

acid-ionization constant, *Ka*

equilibrium constant for the ionization of a weak acid

acidic

describes a solution in which $[H3O+] > [OH-]$

Actinide

Inner transition metal in the bottom of the bottom two rows of the periodic table

active electrode

electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

activity series

A list of elements that will replace elements below them in single-replacement reactions.

Actual yield

amount of product formed in a reaction

Adhesive force

force of attraction between molecules of different chemical identities

Alkali metal

element in group 1

Alkaline batteries

primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

Alkaline earth metal

element in group 2

Alloy

solid mixture of a metallic element and one or more additional elements

Alpha particle (α particle)

positively charged particle consisting of two protons and two neutrons

Amontons's law

(also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Amphiphilic

molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

amphiprotic

Able to both donate and accept a proton, and thus able to react both as an acid and a base

amphoteric

species that can act as either an acid or a base

Amplitude

extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

Analyte

chemical species of interest; in a titration experiment, it is the solution of unknown solution for which you would like to determine either the concentration of the equilibrium constant.

angular momentum quantum number

quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

Anion

negatively charged atom or molecule (contains more electrons than protons)

anode

electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

Aqueous solution

solution for which water is the solvent

Arrhenius acid

An acid as a compound that dissolves in water to produce H+ ions (hydronium ions, H3O+)

Arrhenius base

a compound that dissolves in water to to yield hydroxide ions (OH−)

Atmosphere

unit of pressure; 1 atm = 101,325 Pa

atom

smallest particle of an element that can enter into a chemical combination

Atomic mass

average mass of atoms of an element, expressed in amu

Atomic mass unit (amu)

(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to 1/12 the mass of a 12C atom

Atomic number (Z)

number of protons in the nucleus of an atom

atomic orbital

mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

Aufbau principle

procedure in which the electron configuration of the elements is determined by “building” them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

average rate

rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

Avogadro's law

volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Avogadro's number (NA)

experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022 × 1023 mol−1

Axial position

location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

Balanced equation

chemical equation with equal numbers of atoms for each element in the reactant and product

Bar

(bar or b) unit of pressure; 1 bar = 100,000 Pa

Barometer

device used to measure atmospheric pressure

Base

substance that produces OH− when dissolved in water

base dissociation constant, (Kb)

is an equilibrium constant that measures how completely a base dissociates into ions in water. The greater the Kb, the stronger the base.

base-ionization constant (*K*b)

equilibrium constant for the ionization of a weak base

basic

describes a solution in which [H3O+] < [OH−]

battery

galvanic cell or series of cells that produces a current; in theory, any galvanic cell

Binary acid

compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H+ ions when dissolved in water)

Binary compound

compound containing two different elements.

Blackbody

idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

Bohr's model

structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

Boiling point

temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Boiling point elevation

elevation of the boiling point of a liquid by addition of a solute

Boiling point elevation constant

the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

bomb calorimeter

device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

Bond angle

angle between any two covalent bonds that share a common atom

Bond dipole moment

separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

Bond distance

(also, bond length) distance between the nuclei of two bonded atoms

Bond energy

(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Bond length

distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

Born-Haber cycle

thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

Boyle's law

volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Brønsted-Lowry acid

A compound that donates a proton to another compound

Brønsted-Lowry base

a compound that accepts a proton

Buret

device used for the precise delivery of variable liquid volumes, such as in a titration analysis

calories (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

calorimeter

device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry

process of measuring the amount of heat involved in a chemical or physical process

Capillary action

flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

cathode

electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cathodic protection

method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

Cation

positively charged atom or molecule (contains fewer electrons than protons)

cell notation

shorthand way to represent the reactions in an electrochemical cell

cell potential

created when two dissimilar metals are connected together and is a measure of the energy per unit charge available from the oxidation-reduction reaction

Celsius (°C)

Unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale.

Chalcogen

element in group 16

Charles's law

volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

chemical change

change producing a different kind of matter from the original kind of matter

Chemical equation

symbolic representation of a chemical reaction

chemical property

behavior that is related to the change of one kind of matter into another kind of matter

Chemical symbol

one-, two-, or three-letter abbreviation used to represent an element or its atoms

chemical thermodynamics

area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

chemistry

Study of the composition, properties, and interactions of matter

Clausius-Clapeyron equation

mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

Coefficient

number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

Cohesive force

force of attraction between identical molecules

Colligative property

property of a solution that depends only on the concentration of a solute species

Colloid

(also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

Combustion analysis

gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

Combustion reaction

vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

common ion effect

effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

Complete ionic equation

chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

composition reaction

A chemical reaction in which a single substance is produced from multiple reactants.

compounds

pure substance that can be decomposed into two or more elements

Compressibility factor (Z)

ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

Concentrated

qualitative term for a solution containing solute at a relatively high concentration

Concentration

quantitative measure of the relative amounts of solute and solvent present in a solution

Condensation

change from a gaseous to a liquid state

conjugate acid

the product that results when a base accepts a proton

conjugate base

the product that remains after an acid donates a proton

Continuous spectrum

electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

coordinate covalent bond

(also, dative bond) bond formed when one atom provides both electrons in a shared pair

core electrons

electron in an atom that occupies the orbitals of the inner shells

Corrosion

degradation of metal through an electrochemical process

Covalent bond

attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

Covalent compound

(also, molecular compound) composed of molecules formed by atoms of two or more different elements

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

Crenation

process whereby biological cells become shriveled due to loss of water by osmosis

Critical point

temperature and pressure above which a gas cannot be condensed into a liquid

Cubic centimeter

Volume of a cube with an edge length of exactly 1 cm.

Cubic meter

SI unit of volume.

d orbitals

written as: *d* orbitals
region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a d electron

Dalton (Da)

alternative unit equivalent to the atomic mass unit

Dalton’s atomic theory

set of postulates that established the fundamental properties of atoms

Dalton’s law of partial pressures

total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

decomposition reaction

A chemical reaction in which a single substance becomes more than one substance.

degeneracy

electron orbitals having the same energy levels

Density

Ratio of mass to volume for a substance or object.

Deposition

change from a gaseous state directly to a solid state

diatomic molecules

molecules that contain two identical atoms chemically bonded together

Diffusion

movement of an atom or molecule from a region of relatively high concentration to one of relatively low concentration (discussed in this chapter with regard to gaseous species, but applicable to species in any phase)

Dilute

qualitative term for a solution containing solute at a relatively low concentration

Dilution

process of adding solvent to a solution in order to lower the concentration of solutes

Dimensional analysis

(also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Dipole moment

property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

dipole-dipole attraction

intermolecular attraction between two permanent dipoles

diprotic acid

A diprotic acid is an acid that yields two H+ ions per acid molecule. Examples of diprotic acids are sulfuric acid, H2SO4, and carbonic acid, H2CO3

Dispersed phase

substance present as relatively large solid or liquid particles in a colloid

Dispersion force

(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

Dispersion medium

solid, liquid, or gas in which colloidal particles are dispersed

Dissociation

physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

Dissolved

describes the process by which solute components are dispersed in a solvent

Double bond

covalent bond in which two pairs of electrons are shared between two atoms

double-replacement reaction

A chemical reaction in which parts of two ionic compounds are exchanged.

dry cell

primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

Dynamic equilibrium

state of a system in which reciprocal processes are occurring at equal rates

effective nuclear charge, *Zeff*

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

Effusion

transfer of gaseous atoms or molecules from a container to a vacuum through very small openings

electric charge

physical property of an object that causes it to be attracted toward or repelled from another charged object; each charged object generates and is influenced by a force called an electric force

electric forces

noncontact force observed between electrically charged objects

electrolysis

process using electrical energy to cause a nonspontaneous process to occur

electrolytes

substances that produce ions when dissolved in water and whose aqueous solutions can conduct electricity

electrolytic cells

electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

Electromagnetic radiation

energy transmitted by waves that have an electric-field component and a magnetic-field component

Electromagnetic spectrum

range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

Electron

negatively charged, subatomic particle of relatively low mass located outside the nucleus

electron affinity

energy required to add an electron to a gaseous atom to form an anion

electron configurations

electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Electron-pair geometry

arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

Electronegativity

tendency of an atom to attract electrons in a bond to itself

electroplating

depositing a thin layer of one metal on top of a conducting surface

electrostatic attraction

phenomenon of two objects with opposite charges attracting each other

electrostatic repulsion

phenomenon of two objects with like charges repelling each other

elements

substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

Empirical formula mass

sum of average atomic masses for all atoms represented in an empirical formula

empirical formulas

simplest or most reduced ratio of elements in a compound

Emulsifying agent

amphiphilic substance used to stabilize the particles of some emulsions

Emulsion

colloid formed from immiscible liquids

End point

measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

endothermic process

chemical reaction or physical change that absorbs heat

Energy

capacity to supply heat or do work

enthalpy (H)

sum of a system’s internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)

heat released or absorbed by a system under constant pressure during a chemical or physical process

Equatorial position

one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

equilibrium constant

value of the reaction quotient for a system at equilibrium

Equivalence point

volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample’s analyte according to the titration reaction

Exact number

Number derived by counting or by definition

Excess reactant

reactant present in an amount greater than required by the reaction stoichiometry

Excited state

state having an energy greater than the ground-state energy

exothermic process

chemical reaction or physical change that releases heat

expansion work

work done as a system expands or contracts against external pressure

extensive property

property of a substance that depends on the amount of the substance

factor-label method

versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Fahrenheit

Unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

first law of thermodynamics

internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

formula mass

sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

Free radical

molecule that contains an odd number of electrons

Freezing

change from a liquid state to a solid state

Freezing point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

Freezing point depression

lowering of the freezing point of a liquid by addition of a solute

Freezing point depression constant

(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

Frequency (ν)

number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

fuel cell

devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

Fundamental unit of charge

(also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602 × 10−19 C

Galvanic cells

electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

galvanized iron

method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

gas

state in which matter has neither definite volume nor shape

Gel

colloidal dispersion of a liquid in a solid

Graham’s law of effusion

rates of diffusion and effusion of gases are inversely proportional to the square roots of their molecular masses

Gravimetric analysis

quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

Ground state

state in which the electrons in an atom, ion, or molecule have the lowest energy possible

Group

vertical column of the periodic table

groups

vertical column of the periodic table

Half-reaction

an equation that shows whether each reactant loses or gains electrons in a reaction.

Halogen

element in group 17

Heat (q)

transfer of thermal energy between two bodies

heat capacity (C)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

Heisenberg uncertainty principle

It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle.

Hemolysis

rupture of red blood cells due to the accumulation of excess water by osmosis

Henry’s law

law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

Hertz (Hz)

the unit of frequency, which is the number of cycles per second, s−1

Hess’s law

if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

heterogeneous equilibrium

equilibria between reactants and products in different phases

heterogeneous mixture

combination of substances with a composition that varies from point to point

homogeneous equilibrium

equilibria within a single phase

homogeneous mixture

(also, solution) combination of substances with a composition that is uniform throughout

Hund’s rule

Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.
All of the electrons in singly occupied orbitals have the same spin (to maximize total spin).

hydrocarbons

compound composed only of hydrogen and carbon; the major component of fossil fuels

Hydrogen bonding

occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

Hydrostatic pressure

pressure exerted by a fluid due to gravity

Hypertonic

of greater osmotic pressure

Hypervalent molecule

molecule containing at least one main group element that has more than eight electrons in its valence shell

Hypothesis

Tentative explanation of observations that acts as a guide for gathering and checking information

Hypotonic

of less osmotic pressure

Ideal gas

hypothetical gas whose physical properties are perfectly described by the gas laws

Ideal gas constant (R)

constant derived from the ideal gas equation R = 0.08226 L atm mol−1 K−1 or 8.314 L kPa mol−1 K−1

Ideal gas law

relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

Ideal solution

solution that forms with no accompanying energy change

Immiscible

of negligible mutual solubility; typically refers to liquid substances

Indicator

substance added to the sample in a titration analysis to permit visual detection of the end point

Induced dipole

temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

Inert electrodes

electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

Inert gas

(also, noble gas) element in group 18

Inert pair effect

tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

initial rate

instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

Inner transition metal

(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

Insoluble

of relatively low solubility; dissolving only to a slight extent

Instantaneous dipole

temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

instantaneous rate

rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

Intensity

property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

intensive property

property of a substance that is independent of the amount of the substance

Interference pattern

pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

Intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

internal energy (U)

total of all possible kinds of energy present in a substance or substances

Ion

electrically charged atom or molecule (contains unequal numbers of protons and electrons)

Ion pair

solvated anion/cation pair held together by moderate electrostatic attraction

ion-dipole attraction

electrostatic attraction between an ion and a polar molecule

ion-product constant for water (*K*w)

equilibrium constant for the autoionization of water

Ionic bond

electrostatic forces of attraction between the oppositely charged ions of an ionic compound

Ionic compound

compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

ionization energy

energy required to remove an electron from a gaseous atom or ion; the associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X2+)

isoelectronic

group of ions or atoms that have identical electron configurations

Isotonic

of equal osmotic pressure

Isotopes

atoms that contain the same number of protons but different numbers of neutrons

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m2/s and 4.184 J = 1 cal

Kc

equilibrium constant for reactions based on concentrations of reactants and products

Kelvin (K)

SI unit of temperature; 273.15 K = 0 ºC

Kilogram (kg)

Standard SI unit of mass; 1 kg = approximately 2.2 pounds

kinetic energy

energy of a moving body, in joules, equal to \frac{1}{2}mv^2 (where m = mass and v = velocity)

Kinetic molecular theory

theory based on simple principles and assumptions that effectively explains ideal gas behavior

KP

written as: KP
equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

Lanthanide

inner transition metal in the top of the bottom two rows of the periodic table

lattice energy

energy required to separate one mole of an ionic solid into its component gaseous ions

Law

Statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world.

law of conservation of matter

when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

Law of constant composition

(also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

Law of definite proportions

(also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

law of mass action

when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Law of multiple proportions

when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Le Châtelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

lead acid battery

secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

Length

Measure of one dimension of an object

Lewis acid

any species that can accept a pair of electrons and form a coordinate covalent bond

Lewis acid-base adduct

compound or ion that contains a coordinate covalent bond between a Lewis acid and a Lewis base

Lewis base

any species that can donate a pair of electrons and form a coordinate covalent bond

Lewis structure

diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol

symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

Limiting reactant

reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

Line spectrum

electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

Linear

shape in which two outside groups are placed on opposite sides of a central atom

liquid

state of matter that has a definite volume but indefinite shape

Liter (L)

Also known as cubic decimeter. Unit of volume; 1 L = 1,000 cm3

Lithium ion batteries

very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

London dispersion force

(also, dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

Lone pair

two (a pair of) valence electrons that are not used to form a covalent bond

Macroscopic domain

Realm of everyday things that are large enough to sense directly by human sight and touch.

magnetic quantum number

quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of ml but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

Main-group element

(also, representative element) element in columns 1, 2, and 12–18

Manometer

device used to measure the pressure of a gas trapped in a container

mass

fundamental property indicating amount of matter

Mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

Mass percentage

ratio of solute-to-solution mass expressed as a percentage

mass-mass calculations

A calculation in which you start with a given mass of a substance and calculate the mass of another substance involved in the chemical equation.

mass-volume percent

ratio of solute mass to solution volume, expressed as a percentage

Matter

anything that occupies space and has mass

Mean free path

average distance a molecule travels between collisions

Melting

change from a solid state to a liquid state

Melting point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

Metal

element that is shiny, malleable, good conductor of heat and electricity

Metalloid

element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

Meter (m)

Standard metric and SI unit of length; 1 m = approximately 1.094 yards

Microscopic domain

Realm of things that are much too small to be sensed directly.

Milliliter (mL)

1/1,000 of a liter; equal to 1 cm3

Minerals

solid materials that occur in the earth

Miscible

mutually soluble in all proportions; typically refers to liquid substances

mixture

matter that can be separated into its components by physical means

Molality (m)

a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

Molar mass (g/mol)

the mass in grams of 1 mole of that substance

molar solubility

solubility of a compound expressed in units of moles per liter (mol/L)

Molarity (M)

unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

Mole

the amount of a substance containing the same number of atoms as the number of atoms in a sample of pure 12C weighing exactly 12 g

Mole fraction (X)

concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

mole-mass calculation

A calculation in which you start with a given number of moles of a substance and calculate the mass of another substance involved in the chemical equation, or vice versa.

Molecular compound

(also, covalent compound) composed of molecules formed by atoms of two or more different elements

Molecular equation

chemical equation in which all reactants and products are represented as neutral substances

molecular formula

true formula for a compound; lists how many atoms of each element are in the compound

Molecular structure

structure that includes only the placement of the atoms in the molecule

molecule

bonded collection of two or more atoms of the same or different elements

monatomic ions

ion composed of a single atom

multiple equilibria

system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

Net ionic equation

chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

neutral solution

The solution in which the concentration of hydroxide ions equals the concentration of hydrogen ions [H3O+] = [OH−]

Neutralization reaction

reaction between an acid and a base to produce salt and water

Neutron

uncharged, subatomic particle located in the nucleus

Nickel-cadmium

(NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

Noble gas

(also, inert gas) element in group 18

Node

any point of a standing wave with zero amplitude

Nomenclature

system of rules for naming objects of interest

Non-polar covalent bond

(also, pure covalent bond) covalent bond between atoms of identical electronegativities

nonelectrolytes

are substances that do not readily ionize (do not produce ions) when dissolved in aqueous (water) solution or in molten state and are poor conductors of electricity.

Nonmetal

element that appears dull, poor conductor of heat and electricity

Normal boiling point

temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

Nucleus

massive, positively charged center of an atom made up of protons and neutrons

nutritional calorie (Calorie)

unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

Octahedral

shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

Octet rule

guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

orbital diagrams

pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

Osmosis

diffusion of solvent molecules through a semipermeable membrane

Osmotic pressure (Π)

opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

overpotential

difference between the theoretical potential and actual potential in an electrolytic cell; the “extra” voltage required to make some nonspontaneous electrochemical reaction to occur

Oxidation

process in which an element’s oxidation number is increased by loss of electrons

Oxidation number

(also, oxidation state) the charge each atom of an element would have in a compound if the compound were ionic

Oxidation-reduction reaction

(also, redox reaction) reaction involving a change in oxidation number for one or more reactant elements

Oxidizing agent

(also, oxidant) substance that brings about the oxidation of another substance, and in the process becomes reduced

Oxyacid

compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H+ ions when dissolved in water)

Oxyanions

polyatomic anion composed of a central atom bonded to oxygen atoms

p orbitals

written as: *p* orbitals
dumbbell-shaped region of space with high electron density, describes orbitals with l = 1. An electron in this orbital is called a p electron

Partial pressure

pressure exerted by an individual gas in a mixture

Partially miscible

of moderate mutual solubility; typically refers to liquid substances

parts per billion (ppb)

ratio of solute-to-solution mass multiplied by 109

parts per million (ppm)

ratio of solute-to-solution mass multiplied by 106

Pascal (Pa)

SI unit of pressure; 1 Pa = 1 N/m2

passivation

It is a widely-used metal finishing process to prevent corrosion

Pauli exclusion principle

specifies that no two electrons in an atom can have the same value for all four quantum numbers

Percent composition

percentage by mass of the various elements in a compound

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Percent yield

measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

Period

(also, series) horizontal row of the periodic table

Periodic law

properties of the elements are periodic function of their atomic numbers.

Periodic table

table of the elements that places elements with similar chemical properties close together

pH

logarithmic measure of the concentration of hydronium ions in a solution

pH scale

The pH scale measures how acidic an object is.

Phase diagram

pressure-temperature graph summarizing conditions under which the phases of a substance can exist

Photon

smallest possible packet of electromagnetic radiation, a particle of light

physical change

change in the state or properties of matter that does not involve a change in its chemical composition

physical property

characteristic of matter that is not associated with any change in its chemical composition

plasma

gaseous state of matter containing a large number of electrically charged atoms and/or molecules

Pnictogen

element in group 15

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

Polar covalent bond

covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

Polar molecule

(also, dipole) molecule with an overall dipole moment

Polarizability

measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

polyatomic ions

ion composed of more than one atom

polymorphs

the ability of a substance to crystallize into different crystalline forms

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

Pounds per square inch (psi)

unit of pressure common in the US

Precipitate

insoluble product that forms from reaction of soluble reactants

Precipitation reaction

reaction that produces one or more insoluble products; when reactants are ionic compounds, sometimes called double-displacement or metathesis

Precision

How closely a measurement matches the same measurement when repeated

Pressure

force exerted per unit area

Primary batteries

single-use nonrechargeable battery

principal quantum number

quantum number specifying the shell an electron occupies in an atom

Product

substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

Proton

positively charged, subatomic particle located in the nucleus

pure substance

homogeneous substance that has a constant composition

Quantitative analysis

the determination of the amount or concentration of a substance in a sample

Quantization

occurring only in specific discrete values, not continuous

quantum mechanics

the study of matter and its interactions with energy on the scale of atomic and subatomic particles. It includes the work of Schrodinger, Heisenberg and other scientists.

Quantum number

integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

Raoult’s law

the partial pressure exerted by a solution component is equal to the product of the component’s mole fraction in the solution and its equilibrium vapor pressure in the pure state

rate expression

mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

Rate of diffusion

amount of gas diffusing through a given area over a given time

rate of reaction

measure of the speed at which a chemical reaction takes place

Reactant

substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

reaction quotient

ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

Reducing agent

(also, reductant) substance that brings about the reduction of another substance, and in the process becomes oxidized

Reduction

process in which an element's oxidation number is decreased by gain of electrons

Representative element

(also, main-group element) element in columns 1, 2, and 12–18

Resonance

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

Resonance forms

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

Resonance hybrid

average of the resonance forms shown by the individual Lewis structures

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

Root mean square velocity (urms)

measure of average velocity for a group of particles calculated as the square root of the average squared velocity

Rounding

Procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

s orbitals

spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an s electron

sacrificial anodes

more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

Salt

Ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide. A neutral chemical compound held together by an ionic bond consisting of positively charged cations and negatively charged anions.

Saturated

of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

Scientific method

Path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory.

Scientific Notation

method to simplify very large and very small numbers by utilizing a base 10 exponential methodology

Second (s)

Standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

Secondary batteries

battery that can be recharged

selective precipitation

process in which ions are separated using differences in their solubility with a given precipitating reagent

Semipermeable membrane

a membrane that selectively permits passage of certain ions or molecules

Series

(also, period) horizontal row of the period table

shells

set of orbitals with the same principal quantum number, n

SI units (International System of Units)

Standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

significant digits

(also, significant figures) all of the measured digits in a determination, including the uncertain last digit

Significant figures

(also, significant digits) all of the measured digits in a determination, including the uncertain last digit

Single bond

bond in which a single pair of electrons is shared between two atoms

Single-displacement reaction

(also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

single-replacement reaction

A chemical reaction in which one element is substituted for another element in a compound.

solid

state of matter that is rigid, has a definite shape, and has a fairly constant volume

Solubility

extent to which a solute may be dissolved in water, or any solvent

solubility product (*K*sp)

equilibrium constant for the dissolution of a slightly soluble electrolyte

Soluble

of relatively high solubility; dissolving to a relatively large extent

Solute

solution component present in a concentration less than that of the solvent

solution

Another name for a homogeneous mixture

Solvation

exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

Solvent

solution component present in a concentration that is higher relative to other components

species (chemical)

can be a group of atoms, molecules, ions etc. that are chemically identical

specific heat capacity (c)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

Spectator ion

ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

spin quantum number

number specifying the electron spin direction, either +1/2 or -1/2

Spontaneous process

physical or chemical change that occurs without the addition of energy from an external source

standard cell potential

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 M for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

Standard conditions of temperature and pressure (STP)

273.15 K (0 °C) and 1 atm (101.325 kPa)

Standard enthalpy of combustion

heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation

enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

Standard molar volume

volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

standard state

set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Standing wave

(also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

state function

property depending only on the state of a system, and not the path taken to reach that state

static electricity

buildup of electric charge on the surface of an object; the arrangement of the charge remains constant ("static")

Stock system

The system of indicating a cation's charge with roman numerals.

Stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

Stoichiometry

relationships between the amounts of reactants and products of a chemical reaction

stress

change to a reaction’s conditions that may cause a shift in the equilibrium

Strong acid

acid that reacts completely when dissolved in water to yield hydronium ions

Strong base

base that reacts completely when dissolved in water to yield hydroxide ions

Strong electrolyte

a substance that dissociates or ionizes completely when dissolved in water and can conduct electricity.

structural formula

shows the atoms in a molecule and how they are connected

Sublimation

change from solid state directly to gaseous state

subshell

set of orbitals in an atom with the same values of n and l

Supercritical fluid

substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

Supersaturated

of concentration that exceeds solubility; a nonequilibrium state

Surface tension

energy required to increase the area, or length, of a liquid surface by a given amount

surroundings

all matter other than the system being studied

Symbolic domain

Specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations.

system

portion of matter undergoing a chemical or physical change being studied

Temperature

ntensive property of matter that is a quantitative measure of "hotness" and "coldness"

Tetrahedral

shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

Theoretical yield

amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Theory

Well-substantiated, comprehensive, testable explanation of a particular aspect of nature.

Thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

titrant

is the "known" solution which has a precise and accurate concentration. It is placed in the buret during a titration experiment

titration

a technique where a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the know solution) is added from a buret to a known quantity of the analyte (the unknown solution) until the reaction is complete.

Titration analysis

quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

Torr

unit of pressure

Transition metal

element in columns 3–11

Trigonal bipyramidal

shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

Trigonal planar

shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

Triple bond

bond in which three pairs of electrons are shared between two atoms

Triple point

temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

Tyndall effect

scattering of visible light by a colloidal dispersion

Uncertainty

Estimate of amount by which measurement differs from true value

Unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

Unit

Sandard of comparison for measurements

Unit conversion factor

Ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

Unsaturated

of concentration less than solubility

valence electrons

electrons in the outermost or valence shell (highest value of n) of a ground-state atom; determine how an element reacts

valence shell

outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest n level (s and p subshells) are in the valence shell, while for transition metals, the highest energy s and d subshells make up the valence shell and for inner transition elements, the highest s, d, and f subshells are included

Valence Shell Electron-Pair Repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

Van der Waals equation

modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

van der Waals forces

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

van’t Hoff factor (i)

the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Vapor pressure

(also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

Vapor pressure of water

pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

Vaporization

change from liquid state to gaseous state

Vector

quantity having magnitude and direction

Viscosity

measure of a liquid's resistance to flow

voltaic cells

another name for a galvanic cell

Volume

Amount of space occupied by an object

Volume percentage

ratio of solute-to-solution volume expressed as a percentage

Wave

oscillation that can transport energy from one point to another in space

Wave-particle duality

term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Wavelength (λ)

distance between two consecutive peaks or troughs in a wave

Weak acid

acid that reacts only to a slight extent when dissolved in water to yield hydronium ions

Weak base

base that reacts only to a slight extent when dissolved in water to yield hydroxide ions

Weak electrolyte

a substance that ionizes only partially when dissolved in water, thus producing an aqueous solution that conducts electricity poorly.

Weight

force that gravity exerts on an object

work (*w*)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

ANCILLARY RESOURCES FOR FACULTY

Suggested Additional Resources

If you are faculty looking for additional resources to support your course delivery using this textbook, there are several options:

- Image PowerPoint Banks (created as part of this project; available below)
- OpenStax Instructor resources for ***Chemistry 2e*** **– OpenStax**
- Homework System: LibreADAPT for OpenStax's ***Chemistry 2e***
- PhET Teaching Resources with suggested activities for simulations

Image PowerPoint Banks

These accessible images banks were created from the text. All numbered figures and tables are included. Attribution and alt-tags are included for each image. If copying or modifying these files, be sure to maintain attribution statements and run the Accessibility checker to ensure files are still accessible.

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Organic Chemistry Supplemental

Most introductory chemistry courses either contain some organic chemistry learning or are followed by a discreet organic chemistry course. There are several organic chemistry resources available through LibreTexts. By January 2024, we hope to release a supplemental text to our Enhanced Introductory College Chemistry text that focuses on organic chemistry and related topics.

Future Updates: Roadmap

In the next released revision, the following updates are proposed:

- Relocation of Indigenous Perspectives and Scientists in Action examples and updated figure numbering
- Updates to media library to reflect alt-tags and captions in chapters

Questions, Comments or Suggestions?

Please let us know if you are using this text or have questions, comments or suggestions. Email our team at OER [at] georgiancollege.ca