

# Introductory Chemistry - Lecture & Lab





# Introductory Chemistry - Lecture & Lab

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This course was developed from generally available open educational resources (OER) in use at multiple institutions, drawing mostly from a primary work published by OpenStax College [Chemistry](https://openstax.org/r/chemistry), but also including additional open works from various sources as noted in attributions on each page of materials.

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# IMPORTANT NOTICE

Dear users,

We regret to inform you that the Achieving the Dream Pressbooks library will be closing permanently at the end of September 2025. We sincerely appreciate the engagement and support this resource has received from our community. To ensure continued access to materials you currently use, we strongly recommend downloading copies of any texts before the closure date.

Multiple download formats are available to accommodate your needs.

Additionally, we encourage you to seek out alternative repositories of OERs such as OpenStax, Creative Commons, and more.

Should you have any questions or concerns regarding this transition, please contact us at [OER@achievingthedream.org](mailto:OER@achievingthedream.org).

Thank you for your understanding and continued support.

Achieving the Dream





PART I

# FACULTY RESOURCES



# I. Lab Manual

Download the [Word file of the Introductory Chemistry Lab Manual](#) here.

Download the [PDF file of the Introductory Chemistry Lab Manual](#) here.

## 2. Request Access

This text is openly licensed and is accessible to all by navigating using the “Contents” menu in the upper left hand corner.

To preserve academic integrity and prevent students from gaining unauthorized access, we have hidden faculty resources and assessments.

Please [contact oer@achievingthedream.org](mailto:contact_oer@achievingthedream.org) to request access to the faculty resources for this course.

Once you have been given access, you'll be able to use the resources provided through the drop down in the upper left hand corner.

### Overview of Faculty Resources

This is a community course developed by an Achieving the Dream grantee. They have either curated or created a collection of faculty resources for this course. Since the resources are openly licensed, you may use them as is or adapt them to your needs.

### Now Available

- Lab Manual
- PDF
- Assignments
- Problem Sets
- Question Banks
- OHM Assessments
- Additional Resources

## Share Your Favorite Resources

If you have sample resources you would like to share with other faculty teaching this course, please send them with an explanatory message and learning outcome alignment to [oeer@achievingthedream.org](mailto:oeer@achievingthedream.org).

## 3. Course Handouts

*The links below are only active in “Preview” mode, which can be accessed by clicking on the “Preview” button in the right navigation. Click on the preview button, and then click on the individual links to download.*

### Periodic Table

[Periodic Table](#) (PDF)

### Significant Figures & Rounding

[Significant Figures & Rounding](#) (.doc file)

### Strong Acids and Bases to Memorize

#### Strong Acids

- HCl (hydrochloric acid)
- HBr (hydrobromic acid)
- HI (hydroiodic acid)
- HNO<sub>3</sub> (nitric acid)
- H<sub>2</sub>SO<sub>4</sub> (sulfuric acid)
- HClO<sub>4</sub> (perchloric acid)
- HClO<sub>3</sub> (chloric acid)

- $\text{HBrO}_4$  (perbromic acid)
- $\text{HClO}_3$  (chloric acid)
- $\text{HIO}_4$  (periodic acid)
- $\text{HClO}_3$  (iodic acid)

If the acid in question is not on this list, you may assume it is weak for this class.

## Strong Bases

- $\text{LiOH}$  (lithium hydroxide)
- $\text{NaOH}$  (sodium hydroxide)
- $\text{KOH}$  (potassium hydroxide)
- $\text{RbOH}$  (rubidium hydroxide)
- $\text{CsOH}$  (cesium hydroxide)
- $\text{Ca(OH)}_2$  (calcium hydroxide)
- $\text{Sr(OH)}_2$  (strontium hydroxide)
- $\text{Ba(OH)}_2$  (barium hydroxide)

If the base in question is not on this list, you may assume it is weak for this class.

## Polyatomic ions

Ions with more than one atom. (You should know the name, formula, and charge!)

Charge	Name	Formula
-1	Acetate	$\text{C}_2\text{H}_3\text{O}_2^-$
-1	Chlorate	$\text{ClO}_3^-$
-1	Chlorite	$\text{ClO}_2^-$
-1	Nitrate	$\text{NO}_3^-$
-1	Nitrite	$\text{NO}_2^-$
-1	Cyanide	$\text{CN}^-$
-1	Hydroxide	$\text{OH}^-$
+1	Ammonium	$\text{NH}_4^+$
-2	Chromate	$\text{CrO}_4^{2-}$
-2	Carbonate	$\text{CO}_3^{2-}$
-2	Sulfate	$\text{SO}_4^{2-}$
-2	Sulfite	$\text{SO}_3^{2-}$
-3	phosphate	$\text{PO}_4^{3-}$
-3	phosphite	$\text{PO}_3^{3-}$



# Solubility Tables

## Soluble

Contains these Ions	Soluble	Exceptions
$\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{NH}_4^+$	Most salts (ionic compounds) containing alkali metals (Group 1) and ammonium are soluble.	none
$\text{NO}_3^-$	Most salts containing nitrate are soluble	
$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$	Most salts containing halogen anions (Main Group 7) are soluble. (Chloride, bromide, and iodide salts)	Salts containing $\text{Cu}^+$ , $\text{Ag}^+$ , $\text{Pb}^{2+}$ , and $\text{Hg}_2^{2+}$
$\text{SO}_4^{2-}$	Many salts containing sulfate are soluble.	Salts containing $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Pb}^{2+}$ , and $\text{Hg}_2^{2+}$

# Insoluble

Contains these Ions	Insoluble	Exceptions
$\text{OH}^-$ and $\text{S}^{2-}$	Most salts containing hydroxide or sulfide anions are insoluble.	Salts containing alkali metals ( $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , and $\text{Cs}^+$ ), and the “heavy” alkaline earth metals ( $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , and $\text{Ba}^{2+}$ )
$\text{CO}_3^{2-}$ , $\text{PO}_4^{3-}$	Most salts containing carbonate or phosphate anions are insoluble.	Salts containing alkali metals (Group 1) and ammonium are soluble. ( $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{NH}_4^+$ )
$\text{SO}_4^{2-}$	Many salts containing sulfate and cations with charges greater than or equal to 2 are insoluble, including salts containing $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Pb}^{2+}$ , and $\text{Hg}_2^{2+}$ .	Salts containing $\text{Cu}^+$ , $\text{Ag}^+$ , $\text{Pb}^{2+}$ , and $\text{Hg}_2^{2+}$
$\text{SO}_4^{2-}$	Many salts containing sulfate are soluble.	Salts containing alkali metals (Group 1) and ammonium are soluble. ( $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{NH}_4^+$ ), and $\text{Mg}^{2+}$

## Oxidation Number Rules

- For pure elements, the oxidation numbers are equal to zero (0).
  - ex:  $\text{Mg}^0 \text{H}_2^0 \text{O}_2^0 \text{Cu}^0$
- For monatomic ions, the oxidation number is equal to the charge on the ion.
  - ex:  $\text{Mg}^{2+} \text{Ca}^{2+} \text{Na}^+ \text{Cu}^+$
- F in compounds is always  $\text{F}^-$  (ox # = -1)
- O in compounds is almost always  $\text{O}^{2-}$  (ox # = -2) (exceptions include peroxides, such as  $\text{H}_2\text{O}_2$ )
- Metals in group 1A are always +1 (ox # = +1)

1. ex:  $\text{Na}^+ \text{K}^+$
6. Metals in group 2A are always +2 (ox # = +2)
  1. ex:  $\text{Mg}^{2+} \text{Ca}^{2+}$
7. H in compounds is usually +1, (unless bonded to a metal, then -1, such as in H-storage materials)  
 $\text{H}_2\text{O}$   $\text{H}^+$   
exception:  $\text{LiBH}_4$  (H is -1)
8. The sum of the oxidation numbers for all atoms in the compound must equal the overall charge of the compound.  
The sum of the oxidation numbers for all atoms in a polyatomic ion must equal the overall charge of the ion.

# 4. Discussion Board Activities

## Discussion Board Standards

It is expected that students will complete the assigned textbook readings prior to posting responses to the discussion board. Student interaction is encouraged. The goal of these online discussions is to simulate the sort of group discussion that can occur in traditional classroom settings. Therefore, students must post comments to at least two classmates. In addition, the instructor may post her reaction to student comments.

Note: The calendar indicates the start and end dates for discussion of particular questions. Students will have a limited period of time to submit their contribution to the discussion board. This will be referred to as the discussion window. When this window closes, students will no longer receive credit for adding their contributions to the discussion.

## Assessment

The instructor will assess the quality of student contributions towards group discussion and determine a grade for each unit/chapter.

1. Student discussion must be relevant to the specific question being discussed.
2. Students should demonstrate their understanding of the issues, theories, and problems from their textbook readings and homework. Good student commentary will make reference to specific textbook readings and make use of the terminology

introduced in the chapter.

3. Students should respond to the discussion questions with an attitude of proper objectivity and a willingness to discuss matters with others who do not share their viewpoint. Criticism of theories or ideas is appropriate; however, the tone of this criticism should remain scholarly rather than personal.
4. Students are encouraged to make use of examples and counter-examples, compare and contrast theories, make reference to past learning, indicate problems or difficulties they have with the theories, and draw out the relevant implications of the discussion.
5. Students may also raise questions they have about the readings and discuss possible answers provided these questions are relevant to the topic of the discussion.

EVERY STUDENT MUST POST AN ANSWER BY STARTING A NEW THREAD. These posts must address all parts of the question, be as long as indicated in the directions for each forum, and be clear and accurate, as well as original. Any copying and pasting of material written by others into the discussion forum is plagiarism. Plagiarism will result in a zero for the assignment; no exceptions.

STUDENTS MUST REPLY TO AT LEAST TWO POSTINGS BY CLASSMATES IN ORDER TO RECEIVE FULL CREDIT. Replies such as “Good posting” or “I agree” will not be considered for full credit—replies must be substantive, detailed and complete. ANY POSTINGS WHICH ARE NOT IN ACADEMIC WRITTEN FORM, AS IN TEXT-MESSAGE FORMAT, WILL RECEIVE A ZERO. EACH MUST BE CHECKED FOR CORRECT SPELLING, GRAMMAR AND PUNCTUATION.

Consider the discussions as opportunities to share ideas about this exciting material with your classmates—enjoy this!

## Introduce Yourself Discussion Activity

Worth 20 points, with replies.

Please write a short paragraph introducing yourself to the class. Be sure to include a photo of yourself (or other representation) in your post. The directions for attaching an image in Blackboard are posted above.

Your introduction must include the following information at a minimum:

- Your name
- Where you currently live and/or where you are from
- Your current educational goals and desired major (subject to change, of course!)
- Reason(s) why you are taking this chemistry course online (as opposed to face-to-face)
- Please include one or more optional topics in your post, which can include hobbies, pets, family, travel dreams, and anything else you'd like to share. 😊

If you need, you can reference this page with [instructions on attaching images to discussion board posts in BlackBoard](#).

## Discovery of the Elements

### **Worth 20 points, with replies**

In this activity, we are going to explore when and where certain elements were discovered (or where the first oldest sample was discovered, in the case of elements known in ancient times). For each element, we will also explore various physical properties and what it is used for currently.

## Assignment

1. **Choose ONE element with an atomic number between 1–57, or 72–86.** You may not choose an element that someone else has chosen, so be sure to check the discussion board before you search and/or post. **Identify your chosen element by name and elemental symbol** (abbreviation shown on the periodic table).
2. **Use online sources to determine when (year) and where the element was discovered. If your chosen element was known in ancient times, record where the first (oldest) sample** was discovered and the era (or range of years) the sample was used. Please try to narrow down the place as much as possible. For instance, a city is better than a region, but a region is preferable to a country.
3. **Watch this video regarding latitude and longitude.**



One or more interactive elements has been excluded from this version of the text. You can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=20#oembed-1>

**Determine and record reasonable latitude and longitude coordinates for where your chosen element was discovered.**

You may use any resources available online, and be sure to include the latitude and longitude coordinates in your post, in addition to the spreadsheet below.

**POST your latitude and longitude coordinates in our shared Google spreadsheet where indicated** (also include your name, your element name, its elemental symbol, and year or era of discovery in the columns provided). We will **create a class map**

**for our elements** after everyone has entered their information into the spreadsheet.

4. **Record the major physical properties of your chosen element in your discussion board post.** Be sure to include information such as the phase in which the element is most commonly observed (i.e., gas, liquid, or solid) and what it looks like. Also include its melting point and boiling point (under normal atmospheric pressure), and its density. (If the substance does not melt, but has a sublimation point instead, then record this information.)
5. **Include in your post a short 3–4 sentence paragraph describing the applications for this element** and/or any environmental or health issues.

Read the posts of at least two other students and post a short comment.

*Be sure to include the links to your source(s).*

## Stoichiometry Inquiry Game

In this discussion board inquiry activity, you will be able to play a “game” designed to help you reinforce your understanding of stoichiometry and limiting reactants.

**Your goals for this activity are as follows:**

1. Predict the amounts of products and leftovers after reaction using the concept of limiting reactant
2. Predict the initial amounts of reactants given the amount of products and leftovers using the concept of limiting reactant
3. Translate from symbolic (chemical formula) to molecular (pictorial) representations of matter
4. Explain how subscripts and coefficients are used to solve limiting reactant problems.



This PDF contains the full instructions for the activity. [Limiting Reactants in Chemical Reactions \(PhET Activity\)](#)

# 5. Discussion Question Rubric

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## Rubric: Discussion Forum Posts

Criteria	Levels of Achievement		
	Proficient	Competent	Novice
Timeliness	Original Thread and 2 replies (at a minimum) are submitted on time. Etiquette and protocol are followed.	Duplicate question posted. Full credit given to student with original placeholder post presented at the earlier publish date. No credit for post student posting second. Will receive credit for replies.	Post is late or replies are late.
Content	Full Credit Content includes all requirements identified in forum instructions. Content and all work is in the correct format and accurate.	Half Credit Content is only partially inclusive of requirements. Minor errors in content may be present. Work may not be shown in correct format.	No credit given to late portion. Content does not focus on requirements.
10 Points	10 Points	5 Points	3 Points
Examples	Examples were included, typed out and work was shown. Examples are shown using the correct format and were both relevant and accurate.	Examples were included but may have had mistakes or been from the incorrect category. Work may not have been complete or in incorrect format.	No examples were included.

---

## Rubric: Discussion Forum Posts

6 Points	6 Points	3 Point	0 Points
Use of Language	Writing is well organized, mechanical elements are error free (grammar, spelling and punctuation)	Writing is somewhat organized with some (minor) mechanical errors.	Writing is not organized or unified. Errors impair communication
6 Points	6 Points	3 Points	1 Point
Replies, Interactions	Replied to two or more other students and replies draw upon original threaded prompts to validate position. Discussion/ responses had depth and related personal experiences or content covered in this unit of instruction. Include work, logic and answer for sample questions in both replies.	Replied to a minimum of two other students and discussion/ responses are somewhat in depth, related to personal experiences or related to prompts in original thread. Questions may have been included but no work was shown or answer was not given for 1 or both replies.	Replied to a minimum of two students with no illustration of understanding of content (example "I agree" simple statements with no support).
8 Points	8 Points	5 Points	2 Points

---

## 6. Instructor Resources from OpenStax College

OpenStax College, the primary source for openly-licensed materials in this course, requests that instructors register and log in to [request access to available instructor resources](#).

Available instructor resources may include items like:

- Getting Started Guide
- Lecture Slides
- Sample Syllabus Language

If you have trouble accessing these materials, [please let us know](#).

### Instructor Solution Manual

Click here to [download the detailed solutions to OpenStax's exercises](#).

# 7. Quizzes Download

Download an import file for all quizzes here: [Chemistry Supplemental Test Items.imscc](#)

## Quiz Index

Here is a list of the quizzes and how many questions there are in each. You can also download the answer keys for all quizzes by clicking on the links below.

1. [Essential Ideas](#), 57 Questions
2. [Atoms, Molecules, and Ions](#), 53 Questions
3. [Composition of Substances and Solutions](#), 49 Questions
4. [Stoichiometry of Chemical Reactions](#), 105 Questions
5. [Thermochemistry](#), 20 Questions
6. [Electronic Structure and Periodic Properties of Elements](#), 38 Questions
7. [Chemical Bonding and Molecular Geometry](#), 61 Questions
8. [Advanced Theories of Covalent Bonding](#), 5 Questions
9. [Gases](#), 28 Questions
10. [Liquids and Solids](#), 18 Questions
11. [Solutions and Colloids](#), 32 Questions
12. [Kinetics](#), 10 Questions
13. [Fundamental Equilibrium Concepts](#), 7 Questions
14. [Acid-Base Equilibria](#), 46 Questions
15. Equilibria of Other Reaction Classes, no test items
16. [Thermodynamics](#), 7 Questions
17. [Electrochemistry](#), 30 Questions
18. [Representative Metals, Metalloids, and Nonmetals](#), 8 Questions
19. Transition Metals and Coordination Chemistry, no test items
20. [Organic Chemistry](#), 1 Question

21. [Nuclear Chemistry](#), 23 Questions

# 8. Problem Sets

## Essential Ideas

- General Concepts
  - [General Concepts Problems](#)
  - [General Concepts Solutions](#)
- Conversions
  - [Conversions Practice Problems](#)
  - [Conversions Solutions](#)
- Significant Figures
  - [Significant Figures Problems](#)
  - [Significant Figures Solutions](#)
- Dimensional Analysis
  - [Dimensional Analysis Practice Problems](#)
  - [Dimensional Analysis Solutions](#)

## Atoms, Molecules, and Ions

- Isotopes
  - [Isotopes Problems](#)
  - [Isotopes Solutions](#)
- Naming Ionic Compounds
  - [Naming Ionic Compounds Problems](#)
  - [Naming Ionic Compounds Solutions](#)
- Formulas for Ionic Compounds
  - [Formulas for Ionic Compounds Problems](#)
  - [Formulas for Ionic Compounds Solutions](#)



- Naming Acids and Covalent Compounds
  - [Naming Acids and Covalent Compounds Problems](#)
  - [Naming Acids and Covalent Compounds Solutions](#)
- Nomenclature
  - [Nomenclature Practice Quiz](#)
  - [Nomenclature Practice Quiz Answer Key](#)

## Composition of Substances and Solutions

- Ionic Compounds and Number of Particles
  - [Ionic Compounds and Number of Particles Problems](#)
  - [Ionic Compounds and Number of Particles Solutions](#)
- Chemical Formulas and Intro to Balancing Equations
  - [Chemical Formulas and Intro to Balancing Equations](#)
  - [Chemical Formulas and Intro to Balancing Equations Solutions](#)
- Balancing Chemical Equations
  - [Balancing Chemical Equations](#)
  - [Balancing Chemical Equations Solutions](#)
- Molar Mass
  - [Calculating Molar Mass Problems](#)
  - [Calculating Molar Mass Solutions](#)
- Conversions and Avogadro's Number
  - [Conversions and Avogadro's Number Problems](#)
  - [Conversions and Avogadro's Number Solutions](#)
- Empirical Formula Calculations and Stoichiometry
  - [Empirical Formula Calculations and Stoichiometry Problems](#)
  - [Empirical Formula Calculations and Stoichiometry Solutions](#)

# Chemical Bonding and Molecular Geometry

- Lewis Structures
  - [Lewis Structures, Bond Lengths/Strengths Problems](#)
  - [Lewis Structures, Bond Lengths/Strengths Solutions](#)
- VSEPR and Molecular Geometry
  - [VSEPR Exam Practice Problems](#)
  - [VSEPR Solutions](#)

## Gases

- Gases (Dalton, KTG, Stoichiometry, van der Waals)
  - [Gases Practice Problems](#)
  - [Gases Practice Problems Solutions](#)
- Gas Laws
  - [Gas Laws Practice Problems](#)
  - [Gas Laws Solutions](#)

## 9. Extra Resources

### Composition of Substances and Solutions

This tutorial by Nauticus covers units of concentration and [examples of how to convert concentration units](#).

### Chemical Bonding and Molecular Geometry

- [This website will help you visualize molecules in 3 dimensions](#).
- [These problems cover the main features of VSEPR](#), but do not address bond angle and distortions due to lone pairs. Be sure to identify the bond angles and any distortions present in the molecules.

# 10. Additional MyOpenMath Quizzes

## MyOpenMath

Quizzes are included in the course, and delivered in the Lumen MyOpenMath platform. You can access and review these questions by signing into [MyOpenMath](#), with the username: **guest** No password is necessary.

The quizzes are listed below:

- Essential Ideas
  - Classification of Matter, 7 Questions
  - Units of Measurement, 10 Questions
  - Temperature, 6 Questions
  - Significant Figures, 8 Questions
  - Scientific Notation, 9 Questions
  - Dimensional Analysis, 9 Questions
  - Essential Ideas Quiz, 11 Questions
- Atoms, Molecules, and Ions
  - Atomic Structure, 10 Questions
  - Periodic Table Organization, 9 Questions
  - Chemical Formulas, 54 Questions
  - Molecular Nomenclature, 52 Questions
  - Atoms, Molecules, and Ions Quiz, 16 Questions
- Composition of Substances and Solutions
  - Atomic Mass, 4 Questions
  - Stoichiometry/The Mole, 7 Questions
  - Percent Composition, 6 Questions
  - Empirical Formulas, 6 Questions

- Composition of Substances and Solutions Quiz, 5 Questions
- Stoichiometry of Chemical Reactions
  - Balancing Chemical Equations, 8 Questions
  - Reaction Stoichiometry, 6 Questions
  - Reaction Yields, 3 Questions
  - Solution Concentration, 4 Questions
  - Solution Concentration (Other Units), 7 Questions
  - Oxidation Numbers, 8 Questions
  - Solubility Rules, 5 Questions
  - Classification of Chemical Reactions, 7 Questions
  - Stoichiometry of Chemical Reactions Quiz, 12 Questions
- Electronic Structure and Periodic Properties of Elements
  - Electromagnetic Spectrum, **Still under development. No questions yet.**
  - Orbital Diagrams, **Still under development. No questions yet.**
  - Electron Configuration, 4 Questions
  - Quantum Numbers, **Still under development. No questions yet.**
  - Periodic Trends, **Still under development. No questions yet.**
  - Electronic Structure and Periodic Properties of Elements Quiz, **Still under development. No questions yet.**
- Chemical Bonding and Molecular Geometry
  - VSEPR, **Still under development. No questions yet.**
  - Bonds, **Still under development. No questions yet.**
  - Chemical Bonding and Molecular Geometry Quiz, **Still under development. No questions yet.**
- Gases
  - Individual Gas Laws, 6 Questions
  - Ideal and Combined Gas Laws, 2 Questions
  - Gas Effusion and Diffusion, 3 Questions
  - Gas Stoichiometry, 3 Questions

- Gases Quiz, 10 Questions
- Thermochemistry
  - Energy, 5 Questions
  - Heat and Work, 3 Questions
  - Calorimetry, 6 Questions
  - Enthalpy, 4 Questions
  - Thermochemistry Quiz, 9 Questions

## II. PDF and EPUB Files

[PDF](#)

[EPUB](#)

## 12. San Jacinto Instructor Resources

[Download assessment materials developed by Jose Nuñez at San Jacinto College.](#) The download includes four quizzes and two exams.



## 13. I Need Help



Need more information about this course? Have questions about faculty resources? Can't find what you're looking for? Experiencing technical difficulties?

We're here to help! Contact [oeer@achievingthedream.org](mailto:oeer@achievingthedream.org) for support.



# PART II

# INTRODUCTION



# 14. Introduction

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.



*Figure 1. Chemical substances and processes are essential for our existence, providing sustenance, keeping us clean and healthy, fabricating electronic devices, enabling transportation, and much more. (credit “left”: modification of work by “vxla”/Flickr; credit “left middle”: modification of work by “the Italian voice”/Flickr; credit “right middle”: modification of work by Jason Trim; credit “right”: modification of work by “gosheshe”/Flickr)*

# 15. Chemistry in Context

## *Learning Objectives*

By the end of this module, 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 endeavors 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 brass—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 behavior 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 endeavored to transform “base metals” such as lead into “noble metals” like gold, and to create elixirs to cure disease and extend life (Figure 1).



Figure 1. 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: Chemical Heritage Foundation)

From alchemy came the historical progressions that led to modern

# Chemistry: The Central Science

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graph TD
    Chem[Chemistry] --- Med[Medicine]
    Chem --- Biol[Biology]
    Chem --- Food[Food Science]
    Chem --- Agric[Agriculture]
    Chem --- Geol[Geology Earth Sciences]
    Chem --- Geochem[Geochemistry]
    Chem --- NucChem[Nuclear Chemistry]
    Chem --- Phys[Physics]
    Chem --- Math[Mathematics]
    Chem --- CompSci[Computer Science]
    Chem --- ChemPhys[Chemical Physics]
    Chem --- Nano[Nanoscience Nanotechnology]
    Chem --- MatSci[Materials Science]
    Chem --- ChemEng[Chemical Engineering]
    Chem --- Biochem[Biochemistry Molecular Biology]
    Med --- Tox[Toxicology]
    Biol --- Biochem
    Food --- EnvSci[Environmental Science]
    Agric --- Geochem
    Geol --- Geochem
    Biochem --- EnvSci
    EnvSci --- Geochem
    Geochem --- NucChem
    NucChem --- Phys
    Phys --- Math
    Math --- CompSci
    CompSci --- ChemPhys
    ChemPhys --- Nano
    Nano --- MatSci
    MatSci --- ChemEng
    ChemEng --- Biochem
  
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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.

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 behavior 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 3).

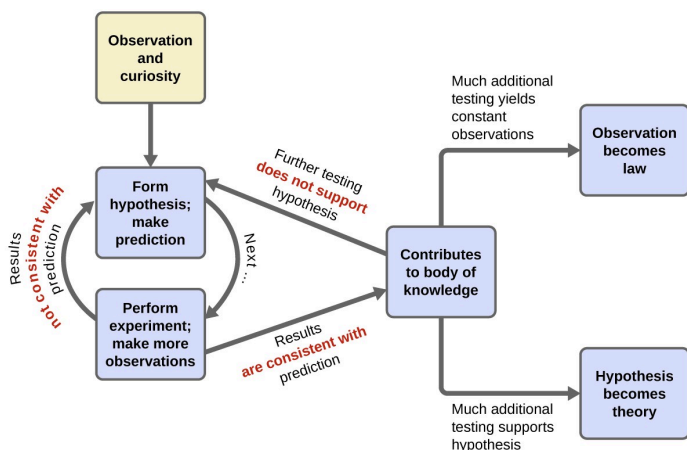


Figure 3. The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

## The Domains of Chemistry

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

**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 everyday 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 color 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 behavior 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 behavior 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 4) 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  $\text{H}_2\text{O}$ , 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.

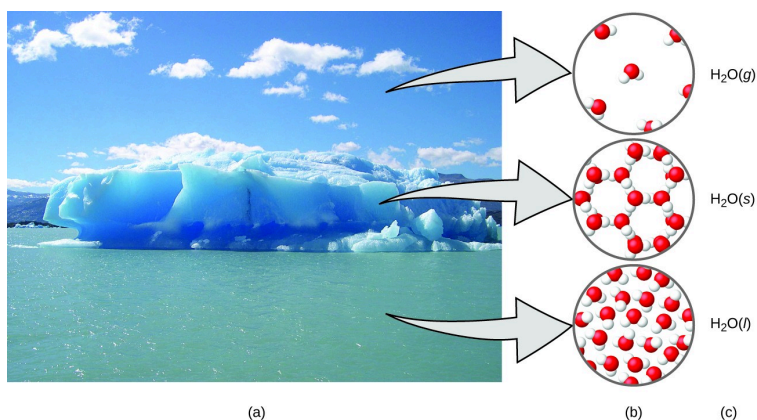


Figure 4. (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula  $\text{H}_2\text{O}$  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 a: modification of work by “Gorkaazk”/Wikimedia Commons)

## Key Concepts and Summary

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 behavior 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.

## *Exercises*

1. Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.
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.
- The pressure of a sample of gas is directly proportional to the temperature of the gas.
  - Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.
  - At a higher temperature, solids (such as salt or sugar) will dissolve better in water.
4. Identify each of the underlined items 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.
- The mass of a lead pipe is 14 lb.
  - The mass of a certain chlorine atom is 35 amu.
  - A bottle with a label that reads Al contains aluminum metal.
  - Al is the symbol for an aluminum atom.
5. Identify each of the underlined items 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 certain molecule contains one H atom and one Cl atom.

- b. Copper wire has a density of about  $8 \text{ g/cm}^3$ .
  - c. The bottle contains 15 grams of Ni powder.
  - d. A sulfur molecule is composed of eight sulfur atoms.
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 behavior? 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 behavior? Explain your answer.

#### Show Selected Answers

1. Place a glass of water outside. It will freeze if the temperature is below  $0^\circ\text{C}$ .
3. (a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)
5. (a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic
7. Macroscopic. The heat required is determined from macroscopic properties.



## Glossary

**chemistry:** study of the composition, properties, and interactions of matter

**hypothesis:** tentative explanation of observations that acts as a guide for gathering and checking information

**law:** statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

**macroscopic domain:** realm of everyday things that are large enough to sense directly by human sight and touch

**microscopic domain:** realm of things that are much too small to be sensed directly

**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

**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

**theory:** well-substantiated, comprehensive, testable explanation of a particular aspect of nature



PART III  
MATTER



# 16. Phases and Classification of Matter

## *Learning Objectives*

By the end of this module, 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). 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.

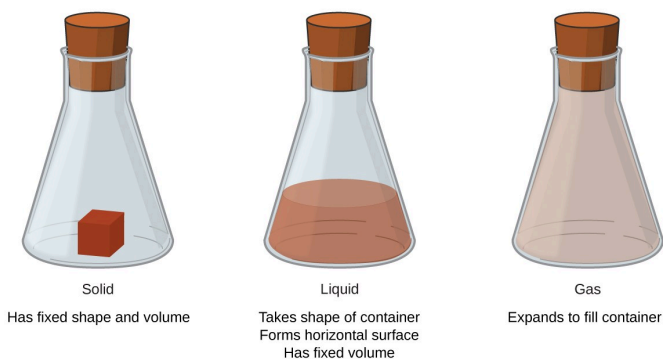


Figure 1. The three most common states or phases of matter are solid, liquid, and gas.

A 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 2). 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 2. A plasma torch can be used to cut metal. (credit: "Hypertherm"/Wikimedia Commons)

In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see. Watch this video to learn more about plasma and the places you encounter it.





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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 3). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring 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.

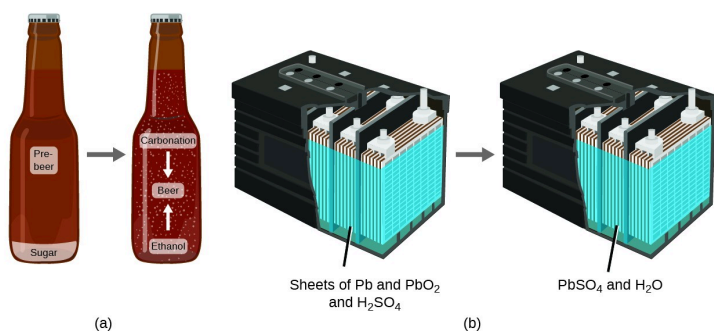


Figure 3. (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

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.

## 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 4). This atom would no longer be gold if it were divided any further.

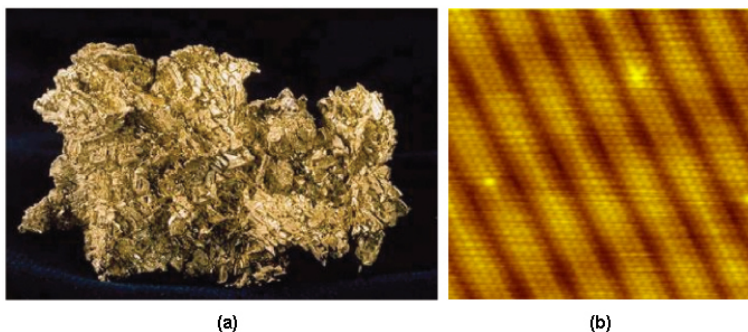


Figure 4. (a) This photograph shows a gold nugget. uniform stripes of light and dark gold, as seen through microscope (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

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 centimeter (0.00001 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 centimeter, 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 5) shows increasingly close microscopic and atomic-level views of ordinary cotton.

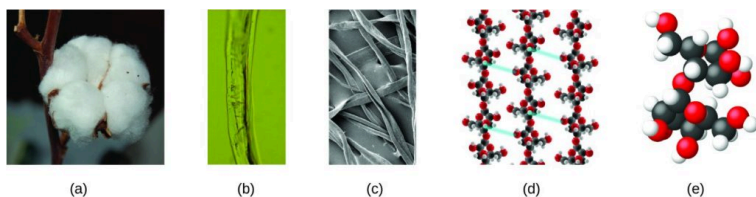


Figure 5. These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by “Featheredtar”/Wikimedia Commons)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about  $3 \times 10^{-13}$  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  $3 \times 10^{14}$ ) 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 6). 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.

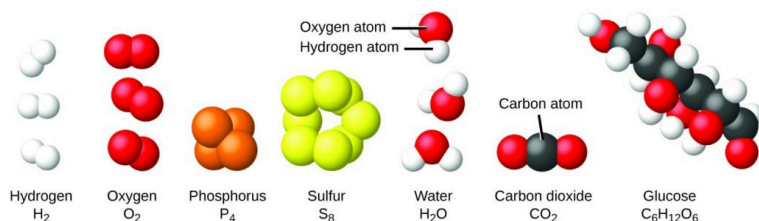


Figure 6. The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

## 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, color, 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 7). 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).

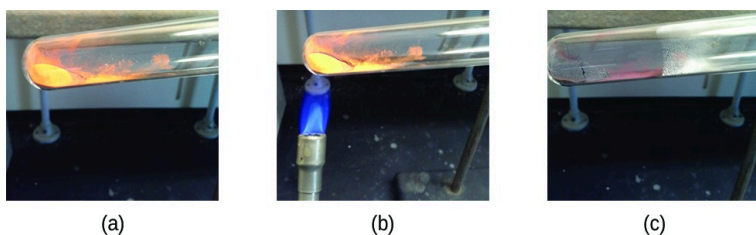


Figure 7. (a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

Many compounds break down when heated. This video shows the breakdown of mercury oxide,  $\text{HgO}$ .



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<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=34#oembed-2>

You can also view an example of the photochemical decomposition of silver chloride ( $\text{AgCl}$ ), the basis of early photography.



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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 colorless 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 8). 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, coloring, flavoring, and electrolytes mixed together uniformly (Figure 8). 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, flavoring, 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 8. (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; credit a “right”: modification of work by Umberto Salvagnin; credit b “left”: modification of work by Jeff Bedford)

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 9).

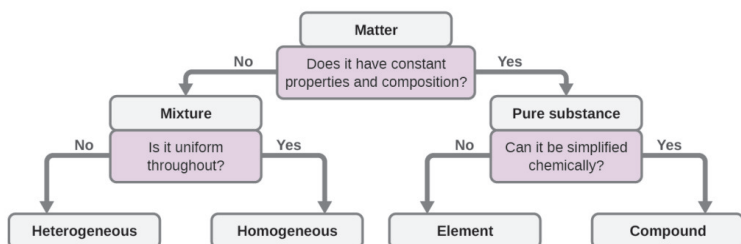


Figure 9. Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth's crust and atmosphere (Table 1). 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.

ElementSymbolPercent Mass

Table 1. Elemental Composition of Earth					
Element	Symbol	Percent Mass			
oxygen	O	49.20	chlorine	Cl	0.19
silicon	Si	25.67	phosphorus	P	0.11
aluminum	Al	7.50	manganese	Mn	0.09
iron	Fe	4.71	carbon	C	0.08
calcium	Ca	3.39	sulfur	S	0.06
sodium	Na	2.63	barium	Ba	0.04
potassium	K	2.40	nitrogen	N	0.03
magnesium	Mg	1.93	fluorine	F	0.03
hydrogen	H	0.87	strontium	Sr	0.02
titanium	Ti	0.58	all others	–	0.47

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 10).

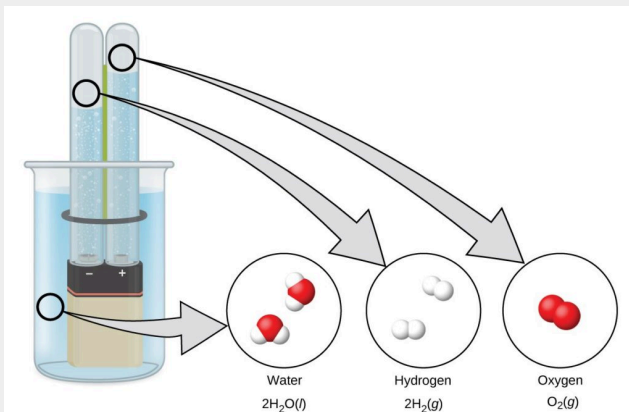
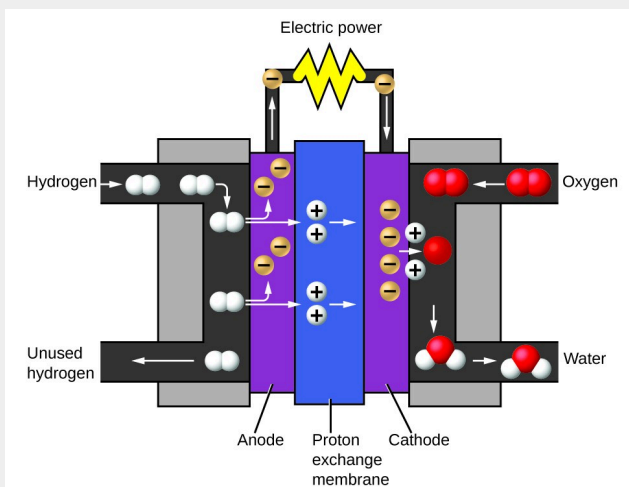


Figure 10. The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid  $\text{H}_2\text{O}$  separates into  $\text{H}_2$  and  $\text{O}_2$  gases.

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,  $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$ , 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 11). 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 11 A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.*

## Chemistry in Everyday Life: Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure 12) 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.

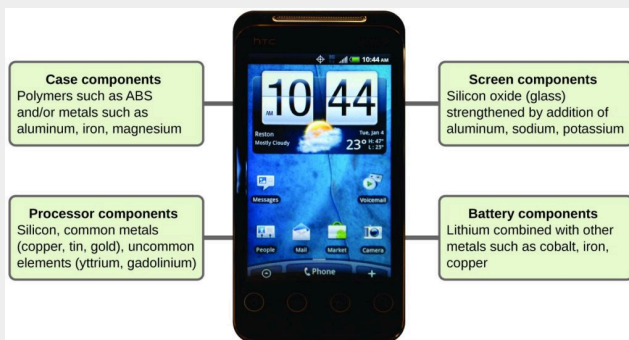


Figure 12. Almost one-third of naturally occurring elements are used to make a cell phone. (credit: modification of work by John Taylor)

## Key Concepts and Summary

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.

## *Exercises*

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?
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?
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?
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.

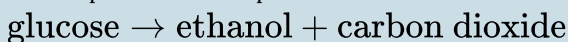
9. Classify each of the following as an element, a compound, or a mixture:
  - a. copper
  - b. water
  - c. nitrogen
  - d. sulfur
  - e. air
  - f. sucrose
  - g. a substance composed of molecules each of which contains two iodine atoms
  - h. gasoline
10. Classify each of the following as an element, 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
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?

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.
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?
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:



- 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?

Show Selected Answers

2. 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.
4. The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.
6. 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.
10. (a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture
12. 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.
14. 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.
16. (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

18. (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

## Glossary

**atom:** smallest particle of an element that can enter into a chemical combination

**compound:** pure substance that can be decomposed into two or more elements

**element:** substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

**gas:** state in which matter has neither definite volume nor shape

**heterogeneous mixture:** combination of substances with a composition that varies from point to point

**homogeneous mixture:** (also, solution) combination of substances with a composition that is uniform throughout

**liquid:** state of matter that has a definite volume but indefinite shape

**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

**mass:** fundamental property indicating amount of matter

**matter:** anything that occupies space and has mass

**mixture:** matter that can be separated into its components by physical means

**molecule:** bonded collection of two or more atoms of the same or different elements

**plasma:** gaseous state of matter containing a large number of electrically charged atoms and/or molecules

**pure substance:** homogeneous substance that has a constant composition

**solid:** state of matter that is rigid, has a definite shape, and has a fairly constant volume

**weight:** force that gravity exerts on an object

# 17. 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
- 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, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, 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 1). 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 color). 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 1. (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 vapor is changed into liquid water. (credit a: modification of work by “95jb14”/Wikimedia Commons; credit b: modification of work by “mjneuby”/Flickr)

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 2). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



(a)



(b)

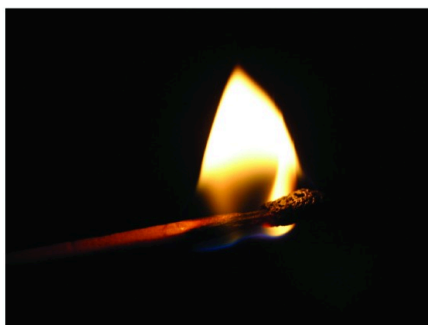
Figure 2. (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by “Atoma”/Wikimedia Commons)

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 3).





(a)



(b)



(c)



(d)

Figure 3. (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 vapor. (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 color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

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 splattered 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 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.

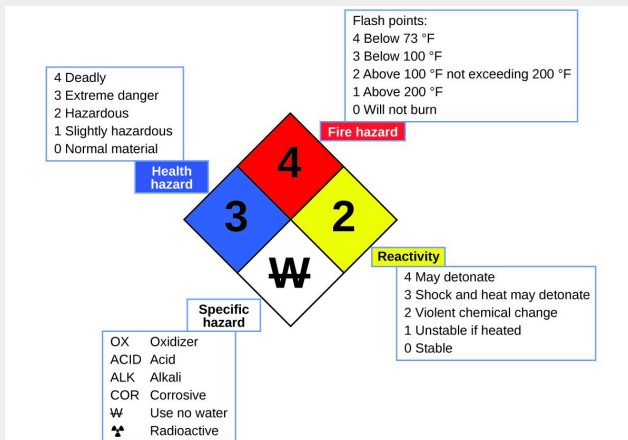


Figure 4. The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

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 behaviors. 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 5). You will learn more about the periodic table as you continue your study of chemistry.

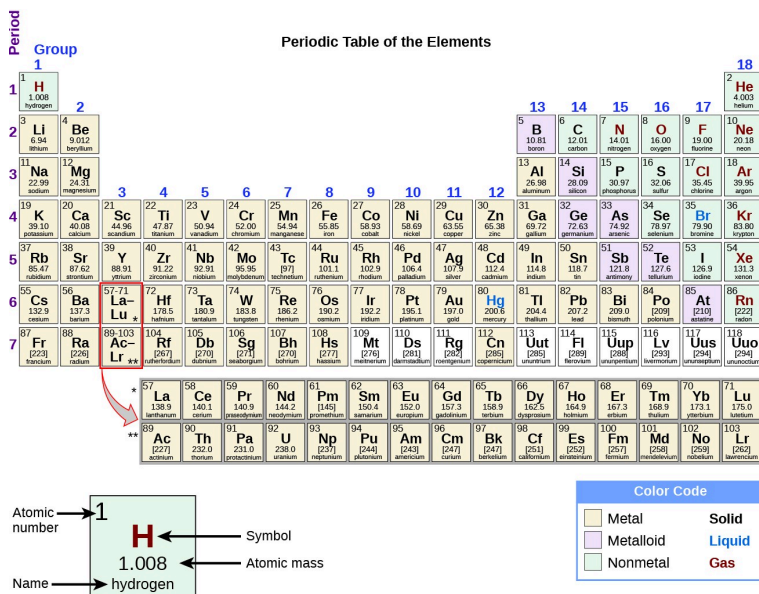


Figure 5. The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

## Key Concepts and Summary

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 as 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.

## *Exercises*

1. Classify the six underlined properties in the following paragraph as chemical or physical: Fluorine is a pale yellow gas that reacts with most substances. The free element melts at  $-220^{\circ}\text{C}$  and boils at  $-188^{\circ}\text{C}$ . 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:
  - a. condensation of steam
  - b. burning of gasoline
  - c. souring of milk
  - d. dissolving of sugar in water
  - e. melting of gold
3. Classify each of the following changes as physical

or chemical:

- a. coal burning
  - b. ice melting
  - c. mixing chocolate syrup with milk
  - d. explosion of a firecracker
  - e. 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?
5. A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?
6. Explain the difference between extensive properties and intensive properties.
7. Identify the following properties as either extensive or intensive.
- a. volume
  - b. temperature
  - c. humidity
  - d. heat
  - e. 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 ( $V$ ). 
$$\text{density} = \frac{\text{mass}}{\text{volume}}; d = \frac{m}{V}.$$
 Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

Selected Answers

2. (a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

4. physical

6. 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.

8. 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).

## Glossary

**chemical change:** change producing a different kind of matter from the original kind of matter

**chemical property:** behavior that is related to the change of one kind of matter into another kind of matter

**extensive property:** property of a substance that depends on the amount of the substance

**intensive property:** property of a substance that is independent of the amount of the substance

**physical change:** change in the state or properties of matter that does not involve a change in its chemical composition



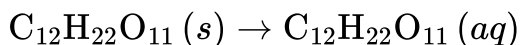
# 18. The Dissolving Process

## *Learning Objectives*

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

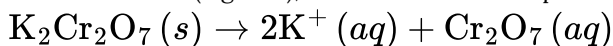
- Describe the basic properties of solutions and how they form
- Predict whether a given mixture will yield a solution based on molecular properties of its components
- Explain why some solutions either produce or absorb heat when they form

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:



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,  $\text{K}_2\text{Cr}_2\text{O}_7$ , is an ionic compound composed of colorless potassium ions,  $\text{K}^+$ , and orange dichromate ions,  $\text{Cr}_2\text{O}_7^{2-}$ . When a small amount of solid potassium chromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (Figure 1), as indicated in this equation:



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 1. When (left) potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) is mixed with (middle) water, it forms (right) a homogeneous orange solution. (credit: modifications of work by Mark Ott)

Visit the [PhET Sugar and Salt Solutions virtual lab](#) to view simulations of the dissolution of common covalent and ionic substances (sugar and salt) in water.

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 1 gives

examples of several different solutions and the phases of the solutes and solvents.

Table 1. Different Types of Solutions		
Solution	Solute	Solvent
air	$\text{O}_2(g)$	$\text{N}_2(g)$
soft drinks <sup>1</sup>	$\text{CO}_2(g)$	$\text{H}_2\text{O}(l)$
hydrogen in palladium	$\text{H}_2(g)$	$\text{Pd}(s)$
rubbing alcohol	$\text{H}_2\text{O}(l)$	$\text{C}_3\text{H}_8\text{O}(l)$ (2-propanol)
saltwater	$\text{NaCl}(s)$	$\text{H}_2\text{O}(l)$
brass	$\text{Zn}(s)$	$\text{Cu}(s)$

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 1.
- 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.

1. If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.

## 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 *favor*, but do not guarantee, the spontaneous formation of a solution:

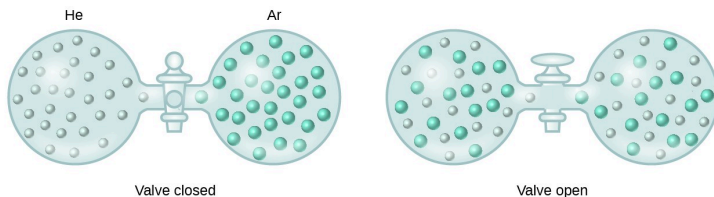
1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increase in the disorder in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

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 behavior) 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 2). 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 2. Samples of helium and argon spontaneously mix to give a solution in which the disorder of the atoms of the two gases is increased.*

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) form ideal solutions, as do mixtures of the hydrocarbons pentane,  $\text{C}_5\text{H}_{12}$ , and hexane,  $\text{C}_6\text{H}_{14}$ . Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in Figure 2 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 3, 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.

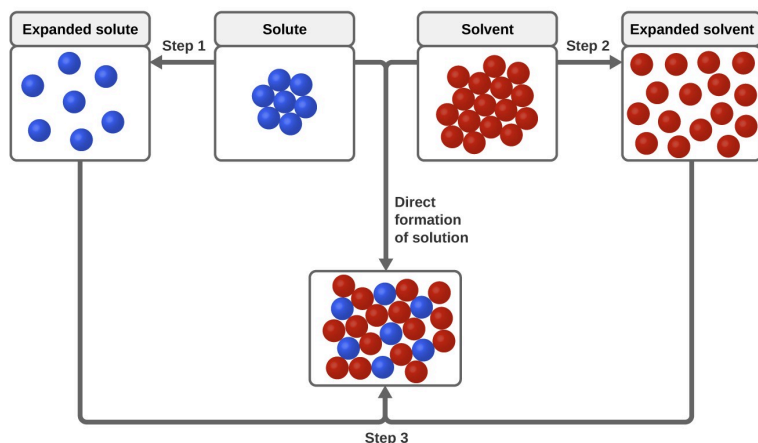


Figure 3. This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

For example, cooking oils and water will not mix to any appreciable extent to yield solutions (Figure 4). 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.



Figure 4. A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra)

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.

On the other hand, a mixture of ethanol and water will mix in any proportions 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 favored, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is one such example and is used to make instant cold packs for treating injuries like the one pictured in Figure 5. A thin-walled plastic bag of water is sealed inside a larger bag with solid  $\text{NH}_4\text{NO}_3$ . When the smaller bag is broken, a solution of  $\text{NH}_4\text{NO}_3$  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 5. An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

Watch this brief video illustrating endothermic and exothermic dissolution processes.





One or more interactive elements has been excluded from this version of the text. You

can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=36#oembed-1>

## *Key Concepts and Summary*

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.

## Exercises

1. How do solutions differ from compounds? From other mixtures?
2. Which of the principal characteristics of solutions can we see in the solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  shown in Figure 1?
3. When  $\text{KNO}_3$  is dissolved in water, the resulting solution is significantly colder than the water was originally.
  - a. Is the dissolution of  $\text{KNO}_3$  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?
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 1.
  - b.  $\text{NO}(\text{l})$  in  $\text{CO}(\text{l})$
  - c.  $\text{Cl}_2(\text{g})$  in  $\text{Br}_2(\text{l})$
  - d.  $\text{HCl}(\text{aq})$  in benzene  $\text{C}_6\text{H}_6(\text{l})$

- e. Methanol  $\text{CH}_3\text{OH}(\text{l})$  in  $\text{H}_2\text{O}(\text{l})$
6. Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane ( $\text{C}_7\text{H}_{16}$ , nonpolar solvent):
- vegetable oil (nonpolar)
  - isopropyl alcohol (polar)
  - 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.
8. Solutions of hydrogen in palladium may be formed by exposing Pd metal to  $\text{H}_2$  gas. The concentration of hydrogen in the palladium depends on the pressure of  $\text{H}_2$  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.
- Determine the molarity of this solution (solution density =  $1.8 \text{ g}/\text{cm}^3$ ).
  - Determine the molality of this solution (solution density =  $1.8 \text{ g}/\text{cm}^3$ ).
  - Determine the percent by mass of hydrogen atoms in this solution (solution density =  $1.8 \text{ g}/\text{cm}^3$ ).

Show Selected Answers

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.

3. The answers are as follows:

- 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.

5. The most important types of intermolecular attractions are as follows:

- a. ion-dipole forces
- b. dipole-dipole forces
- c. dispersion forces
- d. dispersion forces
- e. hydrogen bonding

7. 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.

## Glossary

**alloy:** solid mixture of a metallic element and one or more additional elements

**ideal solution:** solution that forms with no accompanying energy change

**solvation:** exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

**spontaneous process:** physical or chemical change that occurs without the addition of energy from an external source



PART IV

# UNITS AND CONVERSIONS





# 19. Measurements

## *Learning Objectives*

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

- Explain the process of measurement
- Identify the three basic parts of a quantity
- Describe the properties and units of length, mass, volume, density, temperature, and time
- Perform basic unit calculations and conversions in the metric and other unit systems

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behavior 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.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. (Scientific notation is also known as exponential notation). For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as  $2.98 \times 10^5$  kg. The mass of

the average mosquito is about 0.0000025 kilograms, which can be written as  $2.5 \times 10^{-6}$  kg.

**Units**, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter 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 liter. 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 1. 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 1. 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 kilometer because the prefix *kilo* means “one thousand,” which in scientific notation is  $10^3$  (1 kilometer = 1000 m =  $10^3$  m). The prefixes used and the powers to which 10 are raised are listed in Table 2.

Table 2. Common Unit Prefixes			
Prefix	Symbol	Factor	Example
femto	f	$10^{-15}$	1 femtosecond (fs) = $1 \times 10^{-15}$ m (0.0000000000001 m)
pico	p	$10^{-12}$	1 picometer (pm) = $1 \times 10^{-12}$ m (0.000000000001 m)
nano	n	$10^{-9}$	4 nanograms (ng) = $4 \times 10^{-9}$ g (0.000000004 g)
micro	$\mu$	$10^{-6}$	1 microliter ( $\mu$ L) = $1 \times 10^{-6}$ L (0.000001 L)
milli	m	$10^{-3}$	2 millimoles (mmol) = $2 \times 10^{-3}$ mol (0.002 mol)
centi	c	$10^{-2}$	7 centimeters (cm) = $7 \times 10^{-2}$ m (0.07 m)
deci	d	$10^{-1}$	1 deciliter (dL) = $1 \times 10^{-1}$ L (0.1 L)
kilo	k	$10^3$	1 kilometer (km) = $1 \times 10^3$ m (1000 m)
mega	M	$10^6$	3 megahertz (MHz) = $3 \times 10^6$ Hz (3,000,000 Hz)
giga	G	$10^9$	8 gigayears (Gyr) = $8 \times 10^9$ yr (8,000,000,000 Gyr)
tera	T	$10^{12}$	5 terawatts (TW) = $5 \times 10^{12}$ W (5,000,000,000,000 W)

Need a refresher or more practice with scientific notation? Visit [Math Skills Review: Scientific Notation](#) to

go over the basics of scientific notation.

## 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 1); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers ( $1 \text{ km} = 1000 \text{ m} = 10^3 \text{ m}$ ), whereas shorter distances can be reported in centimeters ( $1 \text{ cm} = 0.01 \text{ m} = 10^{-2} \text{ m}$ ) or millimeters ( $1 \text{ mm} = 0.001 \text{ m} = 10^{-3} \text{ m}$ ).

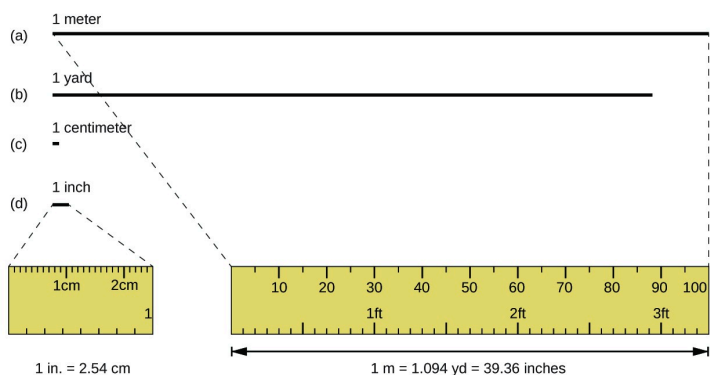


Figure 1. The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

## Mass

The standard unit of mass in the SI system is the **kilogram (kg)**. A kilogram was originally defined as the mass of a liter 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). 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. This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology)*

## 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.

## 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 =  $3 \times 10^{-6}$  and 5 megaseconds = 5,000,000 s =  $5 \times 10^6$  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.

## 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 3). The standard volume is a **cubic meter ( $\text{m}^3$ )**, 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.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter ( $\text{dm}^3$ ). A **liter (L)** is the more common name for the cubic decimeter. One liter is about 1.06 quarts.

A **cubic centimeter ( $\text{cm}^3$ )** is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **cubic**

centimeter) is often used by health professionals. A cubic centimeter is also called a **milliliter (mL)** and is 1/1000 of a liter.

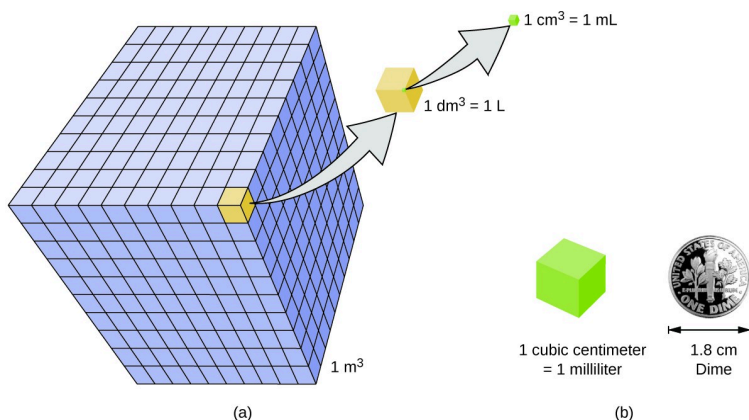


Figure 3. (a) The relative volumes are shown for cubes of 1 m<sup>3</sup>, 1 dm<sup>3</sup> (1 L), and 1 cm<sup>3</sup> (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm<sup>3</sup> (1-mL) cube.

## 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<sup>3</sup>). For many situations, however, this is an inconvenient unit, and we often use grams per cubic centimeter (g/cm<sup>3</sup>) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm<sup>3</sup> (the density of gasoline) to 19 g/cm<sup>3</sup> (the density of gold). The density of air is about 1.2 g/L. Table 3 shows the densities of some common substances.



**Table 3. Densities of Common Substances**

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

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

### *Example 1: 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 centers 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,  $19.3 \text{ g/cm}^3$ . What is the density of lead if a cube of lead has an edge length of  $2.00 \text{ cm}$  and a mass of  $90.7 \text{ g}$ ?

Show Answer

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.

$$\text{volume of lead cube} = 2.00 \text{ cm} \times 2.00 \text{ cm} \times 2.00 \text{ cm} = 8.00 \text{ cm}^3$$

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

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

### *Check Your Learning*

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

Show Answer

1.  $0.599 \text{ cm}^3$
2.  $8.91 \text{ g/cm}^3$

To learn more about the relationship between mass, volume, and density, use this [PhET Density Simulator](#) to

explore the density of different materials, like wood, ice, brick, and aluminum.

### *Example 2: Using Displacement of Water to Determine Density*

This [PhET simulation](#) illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

Show Answer

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{1.25 \text{ L}} = 4.00 \text{ kg/L}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom

of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{10.00 \text{ L}} = 0.500 \text{ kg/L}$$

### *Check Your Learning*

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.

Show Answer

2.00 kg/L

## *Key Concepts and Summary*

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 liters (for volume) and  $\text{g/cm}^3$  (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.

### *Key Equations*

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

### *Exercises*

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?
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
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
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.

Show Selected Answers

2. about a yard

4. (a) kilograms; (b) meters; (c) kilometers/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

6. (a) centi-,  $\times 10^{-2}$ ; (b) deci-,  $\times 10^{-1}$ ; (c) Giga-,  $\times 10^9$ ; (d) kilo-,  $\times 10^3$ ; (e) milli-,  $\times 10^{-3}$ ; (f) nano-,  $\times 10^{-9}$ ; (g) pico-,  $\times 10^{-12}$ ; (h) tera-,  $\times 10^{12}$

## *PhET Simulation Exercises*

1. Visit this [PhET density simulation](#) and select the Same Volume Blocks.
  - a. What are the mass, volume, and density of the yellow block?
  - b. What are the mass, volume and density of the red block?

- c. List the block colors in order from smallest to largest mass.
  - d. List the block colors in order from lowest to highest density.
  - e. How are mass and density related for blocks of the same volume?
2. Visit this [PhET density simulation](#) and select Custom Blocks and then My Block.
  - a. Enter mass and volume values for the block such that the mass in kg is *less than* the volume in L. What does the block do? Why? Is this always the case when mass < volume?
  - b. Enter mass and volume values for the block such that the mass in kg is *more than* the volume in L. What does the block do? Why? Is this always the case when mass > volume?
  - c. How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?
  - d. How would (a) and (b) be different if the liquid in the tank were mercury instead of water?
3. Visit this [PhET density simulation](#) and select Mystery Blocks.
  - a. Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.
  - b. Pick a different Mystery Block and determine its mass, volume, density, and its likely identity.
  - c. Order the Mystery Blocks from least dense to most dense. Explain.

Selected Answers



1. (a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

3. (a) (b) Answer is one of the following. A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold. B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple. C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline. D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond. (c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L) < C/green/ice (0.920 kg/L) < D/red/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

## Glossary

**Celsius (°C):** unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

**cubic centimeter (cm<sup>3</sup> or cc):** volume of a cube with an edge length of exactly 1 cm

**cubic meter (m<sup>3</sup>):** >SI unit of volume

**density:** ratio of mass to volume for a substance or object

**kelvin (K):** SI unit of temperature; 273.15 K = 0° C

**kilogram (kg):** standard SI unit of mass; 1 kg = approximately 2.2 pounds

**length:** measure of one dimension of an object

**liter (L):** (also, cubic decimeter) unit of volume; 1 L = 1,000

$\text{cm}^3$  **meter (m)**: standard metric and SI unit of length; 1 m = approximately 1.094 yards

**milliliter (mL)**: 1/1,000 of a liter; equal to 1  $\text{cm}^3$  **second (s)**: SI unit of time

**SI units (International System of Units)**: standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

**unit**: standard of comparison for measurements

**volume**: amount of space occupied by an object

## 20. Measurement Uncertainty, Accuracy, and Precision

### *Learning Objectives*

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

- Define 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 centimeters, 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.

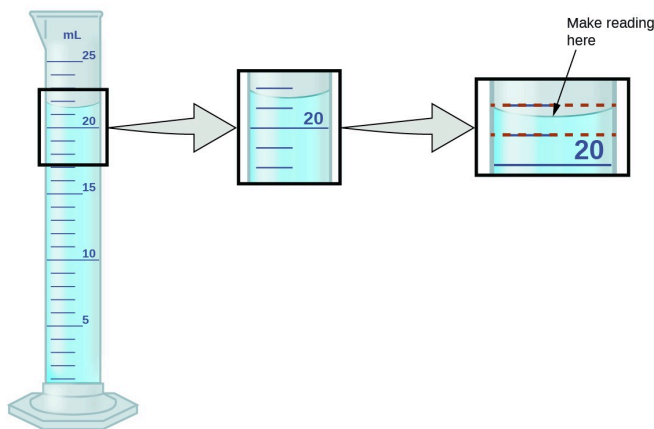


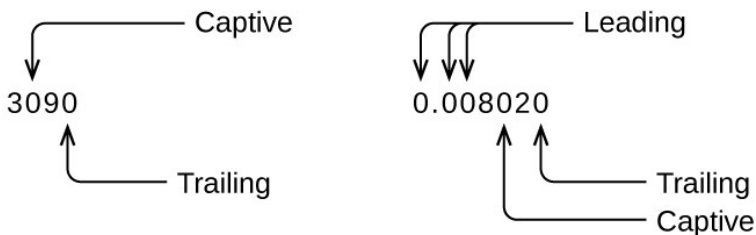
Figure 1. To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in Figure 1. 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

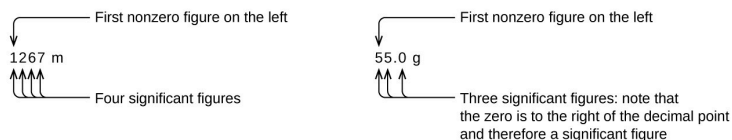
digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale 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  $\pm 0.01$  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, an uncertainty of 0.001 gram. Every measurement has some **uncertainty**, which depends on the device used (and the user's ability). All of the digits in a 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.

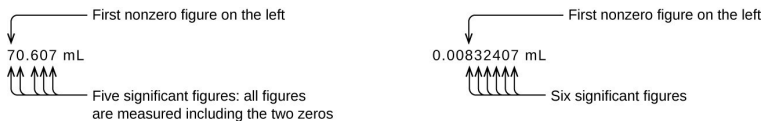
Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought.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



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.



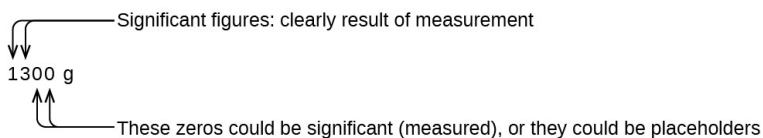
Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as  $8.32407 \times 10^{-3}$ ; 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. The ambiguity can be resolved with the use of exponential notation:  $1.3 \times 10^3$  (two significant figures),  $1.30 \times 10^3$  (three significant figures, if the tens place was measured), or  $1.300 \times 10^3$  (four significant figures, if the ones 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.



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  $3.17 \times 10^8$  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 more than 5, we “round up” and increase the retained digit by 1; if the dropped digit is 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it’s based on reliable statistics and is aimed at avoiding any bias when dropping the digit “5,” since it is equally close to both possible values of the retained digit.)

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, is greater than 5)
- 18.3384 rounds “down” to 18.3 (the dropped digit, 3, is lesser



than 5)

- 6.8752 rounds “up” to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds “down” to 92.8 (the dropped digit is 5, and the retained digit is even)

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

### *Example 1: Rounding Numbers*

Round the following to the indicated number of significant figures:

1. 31.57 (to two significant figures)
2. 8.1649 (to three significant figures)
3. 0.051065 (to four significant figures)
4. 0.90275 (to four significant figures)

Show Answer

1. 31.57 rounds “up” to 32 (the dropped digit is 5, and the retained digit is even)
2. 8.1649 rounds “down” to 8.16 (the dropped digit, 4, is lesser than 5)
3. 0.051065 rounds “down” to 0.05106 (the dropped digit is 5, and the retained digit is even)
4. 0.90275 rounds “up” to 0.9028 (the dropped digit is 5, and the retained digit is even)

## *Check Your Learning*

Round the following to the indicated number of significant figures:

1. 0.424 (to two significant figures)
2. 0.0038661 (to three significant figures)
3. 421.25 (to four significant figures)
4. 28,683.5 (to five significant figures)

Show Answer

1. 0.42
2. 0.00387
3. 421.2
4. 28,684

## *Example 2: 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).

1. Add 1.0023 g and 4.383 g.

2. Subtract 421.23 g from 486 g.

Show Answer

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

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

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

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

$$\begin{array}{r}
 1.0023 \text{ ← Ten thousandths place} \\
 + \quad 4.383 \text{ ← Thousandths place; least precise} \\
 \hline
 5.3853 \\
 \text{Round to thousandths} \nearrow
 \end{array}$$

(a)

$$\begin{array}{r}
 486 \text{ g} \\
 - \quad 421.23 \text{ g} \\
 \hline
 64.77 \text{ g} \\
 \text{Round to ones} \nearrow
 \end{array}
 \longrightarrow \text{Answer is 65 g}$$

(b)

## Check Your Learning

- Add 2.334 mL and 0.31 mL.
- Subtract 55.8752 m from 56.533 m.

Show Answer

1. 2.64 mL
2. 0.658 m

### *Example 3: 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).

1. Multiply 0.6238 cm by 6.6 cm.
2. Divide 421.23 g by 486 mL.

Show Answer

1.  $0.6238 \text{ cm} \times 6.6 \text{ cm} = 4.11708 \text{ cm}^2 \rightarrow$  result is  $4.1 \text{ cm}^2$  (round to two significant figures)  
four significant figures  $\times$  two significant figures  $\rightarrow$  two significant figures answer
2.  $\frac{421.23 \text{ g}}{486 \text{ mL}} = 0.86728 \text{ g/mL} \rightarrow$  result is  $0.867 \text{ g/mL}$  (round to three significant figures)  
 $\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow$  three significant figures answer

### *Check Your Learning*

1. Multiply 2.334 cm and 0.320 cm.
2. Divide 55.8752 m by 56.53 s.

Show Answer

1.  $0.747 \text{ cm}^2$
2.  $0.9884 \text{ m/s}$

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 4: 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.

Show Answer

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

### *Check Your Learning*

What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm<sup>3</sup>?

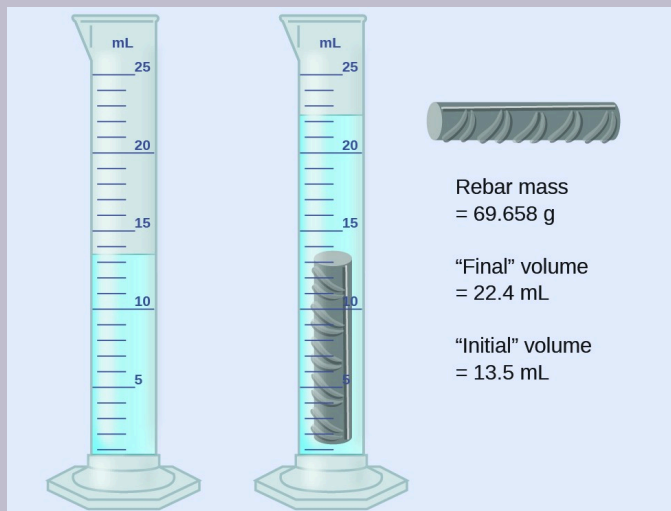
Show Answer

$$1.034 \text{ g/mL}$$

### *Example 5: 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.



1. Use these values to determine the density of this piece of rebar.
2. Rebar is mostly iron. Does your result in number 1 support this statement? How?

Show Answer

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:

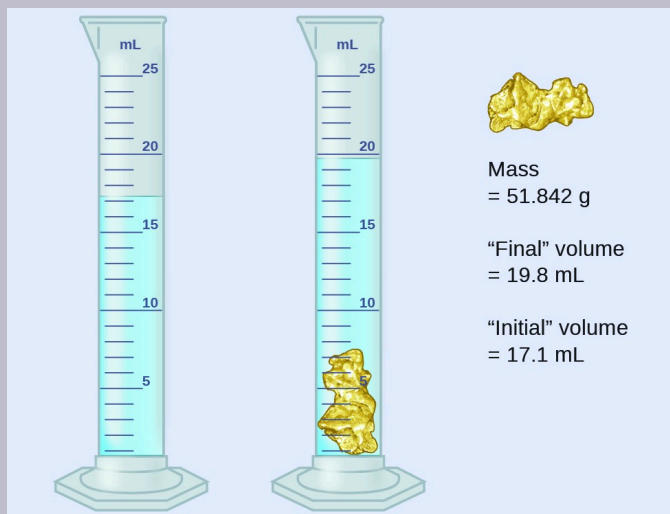
$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658 \text{ g}}{8.9 \text{ cm}^3} = 7.8 \text{ g/cm}^3$$

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

The density of iron is  $7.9 \text{ g/cm}^3$ , very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

### *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.



1. Use these values to determine the density of this

material.

2. Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Show Answer

1.  $19 \text{ g/cm}^3$
2. It is likely gold; the right appearance for gold and very close to the density given for gold in [Measurements](#).

## 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).



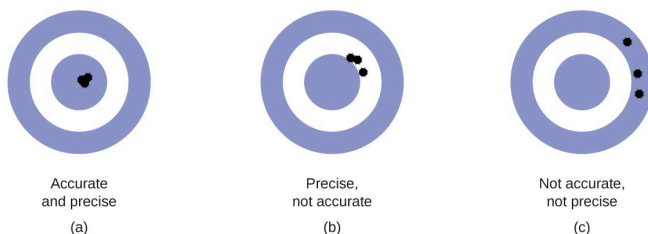


Figure 2. (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

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 1.

**Table 1. 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).

### *Key Concepts and Summary*

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).

### *Exercises*

1. Express each of the following numbers in scientific notation with correct significant figures:
  - a. 711.0
  - b. 0.239
  - c. 90743
  - d. 134.2
  - e. 0.05499

- f. 10000.0
  - g. 0.000000738592
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
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
5. How many significant figures are contained in each of the following measurements?
- a. 38.7 g
  - b.  $2 \times 10^{18}$  m
  - c. 3,486,002 kg
  - d.  $9.74150 \times 10^{-4}$  J
  - e.  $0.0613 \text{ cm}^3$
  - 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.  $2.05 \times 10^8$  m
  - c. 86,002 J
  - d.  $9.740 \times 10^4$  m/s
  - e.  $10.0613 \text{ m}^3$
  - f. 0.17 g/mL
  - g. 0.88400 s
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

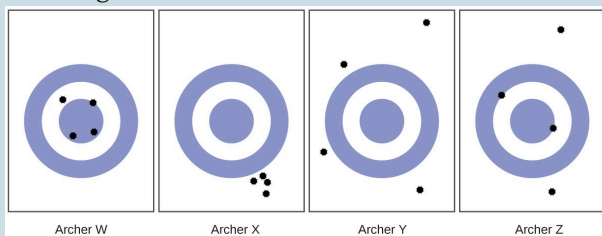
- d. 5.5 ounces
  - e. 473 mL
  - f. 1.75% bismuth
  - g. 0.001% phosphoric acid
  - h. 99.80% inert ingredients
8. Round off each of the following numbers to two significant figures:
- a. 0.436
  - b. 9.000
  - c. 27.2
  - d. 135
  - e.  $1.497 \times 10^{-3}$
  - f. 0.445
9. Round off each of the following numbers to two significant figures:
- a. 517
  - b. 86.3
  - c.  $6.382 \times 10^3$
  - 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.  $628 \times 342$
  - b.  $(5.63 \times 10^2) \times (7.4 \times 10^3)$
  - c. 
$$\begin{array}{r} 28.0 \\ \hline 13.483 \end{array}$$
  - d.  $8119 \times 0.000023$

- e.  $14.98 + 27,340 + 84.7593$
- f.  $42.7 + 0.259$

11. Perform the following calculations and report each answer with the correct number of significant figures.

- a.  $62.8 \times 34$
- b.  $0.147 + 0.0066 + 0.012$
- c.  $38 \times 95 \times 1.792$
- d.  $15 - 0.15 - 0.6155$
- e.  $8.78 \times \left( \frac{0.0500}{0.478} \right)$
- 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?
13. Classify the following sets of measurements as accurate, precise, both, or neither.

- a. Checking for consistency in the weight of chocolate chip cookies: 17.27g, 13.05g, 19.46g, 16.92g
- 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%

Show Selected Answers

2. (a)  $7.04 \times 10^2$ ; (b)  $3.344 \times 10^{-2}$ ; (c)  $5.479 \times 10^2$ ; (d)  $2.2086 \times 10^4$ ; (e)  $1.00000 \times 10^3$ ; (f)  $6.51 \times 10^{-8}$ ; (g)  $7.157 \times 10^{-3}$

4. (a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

6. (a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

8. (a) 0.44; (b) 9.0; (c) 27; (d) 140; (e)  $1.5 \times 10^{-3}$ ; (f) 0.44

10. (a)  $2.15 \times 10^5$ ; (b)  $4.2 \times 10^6$ ; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

12. (a) Archer X; (b) Archer W; (c) Archer Y

## Glossary

**accuracy:** how closely a measurement aligns with a correct value

**exact number:** number derived by counting or by definition

**precision:** how closely a measurement matches the same measurement when repeated

**rounding:** procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

**significant figures:** (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

**uncertainty:** estimate of amount by which measurement differs from true value



## 2I. Unit Conversions and Dimensional Analysis

### *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 ( $\text{m/s} = \text{m/s}$ ). 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 ( $10 \text{ m/s}$ ) 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 ( $\text{m/m/s} = \text{s}$ ) 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,  $\text{m/m}$ ), 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 1.

Table 1. Common Conversion Factors		
Length	Volume	Mass
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft <sup>3</sup> = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	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 centimeters). For example, a basketball player’s vertical jump of 34 inches can be converted to centimeters 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 1: 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 1).

Show Answer

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 centimeters.

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

We write the unit conversion factor in its two forms:

$$\frac{1 \text{ oz}}{28.35 \text{ g}} \text{ and } \frac{28.349 \text{ g}}{1 \text{ oz}}$$

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

$$\begin{aligned} x \text{ oz} &= 125 \cancel{\text{g}} \times \frac{1 \text{ oz}}{28.349 \cancel{\text{g}}} \\ &= \left( \frac{125}{28.349} \right) \text{ oz} \\ &= 4.41 \text{ oz (three significant figures)} \end{aligned}$$

### *Check Your Learning*

Convert a volume of 9.345 qt to liters.

Show Answer

8.844 L

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: 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.

Show Answer

Since **density** =  $\frac{\text{mass}}{\text{volume}}$ , we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A  $\times$  unit conversion factor. The necessary conversion factors are given in Table 1.6: 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 milliliters.

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:**

$$3.78 \cancel{\text{L}} \times \frac{1000 \text{ mL}}{1 \cancel{\text{L}}} = 3.78 \times 10^3 \text{ mL}$$

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:

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

### *Check Your Learning*

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

Show Answer

$$2.956 \times 10^{-2} \text{ L}$$

### *Example 3: 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.

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

Show Answer

#### *Part 1*

We first convert distance from kilometers to miles:

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

Then we 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,

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

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

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

### Part 2

Using the previously calculated volume in gallons, we

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

### Check Your Learning

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?

Show Answer

1. 51 mpg
2. \$62



## Exercises

### Volume

1. 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?
2. 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?
3. How many milliliters of a soft drink are contained in a 12.0-oz can?
4. A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?
5. Many medical laboratory tests are run using 5.0  $\mu\text{L}$  blood serum. What is this volume in milliliters?
6. Milk is sold by the liter in many countries. What is the volume of exactly  $1/2$  gal of milk in liters?
7. Gasoline is sold by the liter in many countries. How many liters are required to fill a 12.0-gal gas tank?
8. Calculate these volumes.
  - a. What is the volume of 11.3 g graphite, density =  $2.25 \text{ g/cm}^3$ ?
  - b. What is the volume of 39.657 g bromine, density =  $2.928 \text{ g/cm}^3$ ?

9. Calculate these volumes.
- What is the volume of 25 g iodine, density =  $4.93 \text{ g/cm}^3$ ?
  - What is the volume of 3.28 g gaseous hydrogen, density =  $0.089 \text{ g/L}$ ?

Show Selected Answers

1.  $\frac{2.0 \text{ L}}{67.6 \text{ fl oz}} = \frac{0.030 \text{ L}}{1 \text{ fl oz}}$

3. 355 mL

5.  $5.0 \times 10^{-3} \text{ mL}$

7. 45.4 L

9. (a) 5.1 mL; (b) 37 L

### *Mass*

- Is a 197-lb weight lifter light enough to compete in a class limited to those weighing 90 kg or less?
- 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?
- If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?
- A long ton is defined as exactly 2240 lb. What is this mass in kilograms?
- The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is  $0.8206 \text{ g/mL}$ , determine the mass in kilograms and pounds of the fuel in a full tank.

6. Calculate these masses.
- What is the mass of  $6.00 \text{ cm}^3$  of mercury, density =  $13.5939 \text{ g/cm}^3$ ?
  - What is the mass of  $25.0 \text{ mL}$  octane, density =  $0.702 \text{ g/cm}^3$ ?
7. Calculate these masses.
- What is the mass of  $4.00 \text{ cm}^3$  of sodium, density =  $0.97 \text{ g/cm}^3$ ?
  - What is the mass of  $125 \text{ mL}$  gaseous chlorine, density =  $3.16 \text{ g/L}$ ?

Show Selected Answers

1. yes; weight =  $89.4 \text{ kg}$   
4.  $1.0160 \times 10^3 \text{ kg}$   
6. (a)  $81.6 \text{ g}$ ; (b)  $17.6 \text{ g}$

### *Length*

- The diameter of a red blood cell is about  $3 \times 10^{-4} \text{ in.}$  What is its diameter in centimeters?
- The distance between the centers of the two oxygen atoms in an oxygen molecule is  $1.21 \times 10^{-8} \text{ cm.}$  What is this distance in inches?
- A chemist's 50-Trillion Angstrom Run (see Exercise 22) would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? ( $1 \text{ \AA} = 1 \times 10^{-8} \text{ cm}$ )
- Many chemistry conferences have held a

50-Trillion Angstrom Run (two significant figures).

How long is this run in kilometers and in miles? ( $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ )

Show Selected Answers

1.  $8 \times 10^{-4} \text{ cm}$

3. 0.46 m; 1.5 ft/cubit

## Exercises

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
2. Write conversion factors (as ratios) for the number of:
  - a. kilometers in 1 mile
  - b. liters in 1 cubic foot
  - c. grams in 1 ounce
3. 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 centimeters and grams?
4. 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 centimeters and grams?

5. Use scientific (exponential) notation to express the following quantities in terms of the SI base units in Table 1:

- a. 0.13 g
- b. 232 Gg
- c. 5.23 pm
- d. 86.3 mg
- e. 37.6 cm
- f. 54  $\mu\text{m}$
- g. 1 Ts
- h. 27 ps
- i. 0.15 mK

6. Complete the following conversions between SI units.

- a. 612 g = \_\_\_\_\_ mg
- b. 8.160 m = \_\_\_\_\_ cm
- c. 3779  $\mu\text{g}$  = \_\_\_\_\_ 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

7. Make the conversion indicated in each of the following:

- a. the men's world record long jump, 29 ft 4 $\frac{1}{4}$  in., to meters

- b. the greatest depth of the ocean, about 6.5 mi, to kilometers
  - c. the area of the state of Oregon,  $96,981 \text{ mi}^2$ , to square kilometers
  - d. the volume of 1 gill (exactly 4 oz) to milliliters
  - e. the estimated volume of the oceans,  $330,000,000 \text{ mi}^3$ , to cubic kilometers.
  - f. the mass of a 3525-lb car to kilograms
  - g. the mass of a 2.3-oz egg to grams
8. 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 kilometers
  - c. the area of an 8.5 t 11-inch sheet of paper in  $\text{cm}^2$
  - d. the displacement volume of an automobile engine,  $161 \text{ in.}^3$ , to liters
  - e. the estimated mass of the atmosphere,  $5.6 \times 10^{15}$  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)
9. 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?

10. To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing  $\frac{1}{4}$  lb is available. Did the student have enough of the compound?
11. A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?
12. 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?
13. 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  $\times$  width  $\times$  length dimensions are 1.50 in.  $\times$  3.50 in.  $\times$  8.00 ft in the US. What are the dimensions in cm  $\times$  cm  $\times$  m?
  - b. This lumber can be used as vertical studs, which are typically placed 16.0 in. apart. What is that distance in centimeters?
14. Calculate the density of aluminum if 27.6 cm<sup>3</sup> has a mass of 74.6 g.
15. Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm<sup>3</sup>?

Show Selected Answers

1. (a)  $\frac{1.0936 \text{ yd}}{1 \text{ m}}$  ; (b)  $\frac{0.94635 \text{ L}}{1 \text{ qt}}$  ; (c)  $\frac{2.2046 \text{ lb}}{1 \text{ kg}}$
3. 68–71 cm; 400–450 g

5. (a)  $1.3 \times 10^{-4}$  kg; (b)  $2.32 \times 10^8$  kg; (c)  $5.23 \times 10^{-12}$  m; (d)  $8.63 \times 10^{-5}$  kg; (e)  $3.76 \times 10^{-1}$  m; (f)  $5.4 \times 10^{-5}$  m; (g)  $1 \times 10^{12}$  s; (h)  $2.7 \times 10^{-11}$  s; (i)  $1.5 \times 10^{-4}$  K

8. (a) 394 ft (b) 5.9634 km (c)  $6.0 \times 10^2$  (d) 2.64 L (e)  $5.1 \times 10^{18}$  kg (f) 14.5 kg (g) 324 mg

9. Yes, the acid's volume is 123 mL.

11. 62.6 in (about 5 ft 3 in.) and 101 lb

13. (a)  $3.81 \text{ cm} \times 8.89 \text{ cm} \times 2.44 \text{ m}$ ; (b) 40.6 cm

14.  $2.70 \text{ g/cm}^3$

## 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,  $0^\circ\text{C}$  is defined as the freezing temperature of water and  $100^\circ\text{C}$  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  $32^\circ\text{F}$  and the boiling temperature as  $212^\circ\text{F}$ . 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, ( $100^{\circ} \text{ C}$ ,  $212^{\circ} \text{ F}$ ) or ( $0^{\circ} \text{ C}$ ,  $32^{\circ} \text{ F}$ ), 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:

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

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  $-273.15\text{ }^{\circ}\text{C}$ . 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:

$$\begin{aligned} T_{\text{K}} &= T_{\circ\text{C}} + 273.15 \\ T_{\circ\text{C}} &= T_{\text{K}} - 273.15 \end{aligned}$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 1 shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.

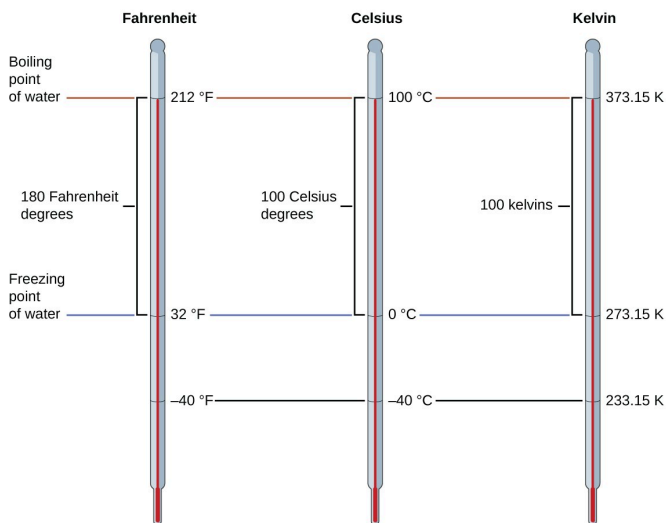


Figure 1. The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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 4: 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?

Show Answer

$$\text{K} = ^\circ\text{C} + 273.15 = 37.0 + 273.2 = 310.2 \text{ K}$$

$$^\circ\text{F} = \frac{9}{5} ^\circ\text{C} + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6^\circ \text{ F}$$

*Check Your Learning*

Convert 80.92 °C to K and °F.

Show Answer

$$354.07 \text{ K}, 177.7^\circ \text{ F}$$

### *Example 5: 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?

Show Answer

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

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

### *Check Your Learning*

Convert 50 °F to °C and K.

Show Answer

10 °C, 280 K

### *Key Concepts and Summary*

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.

#### *Key Equations*

- $T_{\text{°C}} = \frac{5}{9} \times T_{\text{°F}} - 32$
- $T_{\text{°F}} = \frac{9}{5} \times T_{\text{°C}} + 32$

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

## *Exercises*

1. Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.
2. Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.
3. Convert the temperature of the coldest area in a freezer, -10 °F, to degrees Celsius and kelvin.
4. Convert the temperature of dry ice, -77 °C, into degrees Fahrenheit and kelvin.
5. Convert the boiling temperature of liquid ammonia, -28.1 °F, into degrees Celsius and kelvin.
6. 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?
7. 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?

Show Selected Answers

1. 5371 °F, 3239 K
3. -23 °C, 250 K
5. -33.4 °C, 239.8 K

7. 113 °F

## Glossary

**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

**Fahrenheit:** unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

**unit conversion factor:** ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit





PART V

# ATOMS, ELECTRONS AND THE PERIODIC TABLE



## 22. Atomic Structure and Symbolism

### *Learning Objectives*

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

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- 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 1).

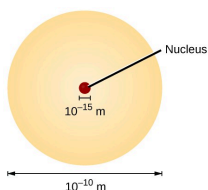


Figure 1. If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by “babyknight”/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than  $2 \times 10^{-23}$  g, and an electron has a charge of less than  $2 \times 10^{-19}$  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” as will be discussed later in this module.) Thus, one amu is exactly  $\frac{1}{12}$  of the mass of one carbon-12 atom:  $1 \text{ amu} = 1.6605 \times 10^{-24}$  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  $e = 1.602 \times 10^{-19}$  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 1. (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, and you will learn about it in the chapter on nuclear chemistry.)

Table 1. Properties of Subatomic Particles					
Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	$-1.602 \times 10^{-19}$	1-	0.00055	$0.00091 \times 10^{-24}$
proton	nucleus	$1.602 \times 10^{-19}$	1+	1.00727	$1.67262 \times 10^{-24}$
neutron	nucleus	0	0	1.00866	$1.67493 \times 10^{-24}$

The number of protons in the nucleus of an atom is its **atomic number (Z)**. This is the defining trait of an element: Its value 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. 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 is

therefore the difference between the mass number and the atomic number:  $A - Z = \text{number of neutrons}$ .

atomic number ( $Z$ ) = number of protons

atomic mass ( $A$ ) = number of protons + number of neutrons

$A - Z = \text{number of neutrons}$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an **ion**. The charge of an atom is defined as follows:

Atomic charge = number of protons – number of electrons

As will be discussed in more detail later in this chapter, 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 ( $Z = 11$ ) has 11 electrons. If this atom loses one electron, it will become a cation with a  $1+$  charge ( $11 - 10 = 1+$ ). A neutral oxygen atom ( $Z = 8$ ) has eight electrons, and if it gains two electrons it will become an anion with a  $2-$  charge ( $8 - 10 = 2-$ ).

### *Example 1: Composition of an Atom*

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2).

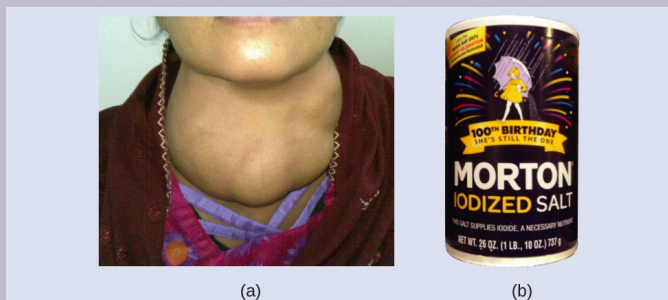


Figure 2. (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by “Almazi”/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a  $1^-$  charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Show Answer

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 ( $127 - 53 = 74$ ). Since the iodine is added as a  $1^-$  anion, the number of electrons is 128 [ $127 - (1^-) = 128$ ].

## Check Your Learning

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Show Answer

78 protons; 117 neutrons; charge is 4+

## 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). 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).

The symbols for several common elements and their atoms are listed in Table 2. 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.



Figure 3. The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.



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](#).

---

**Table 2. Some Common Elements and Their Symbols**

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from <i>ferrum</i> )
bromine	Br	lead	Pb (from <i>plumbum</i> )
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from <i>hydrargyrum</i> )
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from <i>kalium</i> )
copper	Cu (from <i>cuprum</i> )	silicon	Si
fluorine	F	silver	Ag (from <i>argentum</i> )
gold	Au (from <i>aurum</i> )	sodium	Na (from <i>natrium</i> )
helium	He	sulfur	S
hydrogen	H	tin	Sn (from <i>stannum</i> )
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 honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

Visit [this site to learn more about IUPAC, the International Union of Pure and Applied Chemistry](#), and explore its periodic table.

## Isotopes

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 (Figure 4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ , and  $^{26}\text{Mg}$ . These isotope symbols are read as “element, mass number” and can be symbolized consistent with this reading. For instance,  $^{24}\text{Mg}$  is read as “magnesium 24,” and can be written as “magnesium-24” or “Mg-24.”  $^{25}\text{Mg}$  is read as “magnesium 25,” and can be written as “magnesium-25” or “Mg-25.” All magnesium atoms have 12 protons in their nucleus. They differ only because a  $^{24}\text{Mg}$  atom has 12 neutrons in its nucleus, a  $^{25}\text{Mg}$  atom has 13 neutrons, and a  $^{26}\text{Mg}$  has 14 neutrons.

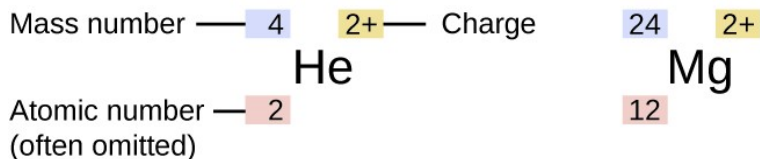


Figure 4. The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 3. 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  ${}^2\text{H}$ , is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized  ${}^3\text{H}$ , is also called tritium and sometimes symbolized T.

**Table 3. Nuclear Compositions of Atoms of the Very Light Elements**

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	${}^1_1\text{H}$ (protium)	1	1	0	1.0078	99.989
	${}^2_1\text{H}$ (deuterium)	1	1	1	2.0141	0.0115
	${}^3_1\text{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	${}^3_2\text{He}$	2	2	1	3.01603	0.00013
	${}^4_2\text{He}$	2	2	2	4.0026	100
lithium	${}^6_3\text{Li}$	3	3	3	6.0151	7.59
	${}^7_3\text{Li}$	3	3	4	7.0160	92.41
beryllium	${}^9_4\text{Be}$	4	4	5	9.0122	100
boron	${}^{10}_5\text{B}$	5	5	5	10.0129	19.9
	${}^{11}_5\text{B}$	5	5	6	11.0093	80.1
carbon	${}^{12}_6\text{C}$	6	6	6	12.0000	98.89
	${}^{13}_6\text{C}$	6	6	7	13.0034	1.11
	${}^{14}_6\text{C}$	6	6	8	14.0032	— (trace)
nitrogen	${}^{14}_7\text{N}$	7	7	7	14.0031	99.63
	${}^{15}_7\text{N}$	7	7	8	15.0001	0.37
oxygen	${}^{16}_8\text{O}$	8	8	8	15.9949	99.757
	${}^{17}_8\text{O}$	8	8	9	16.9991	0.038
	${}^{18}_8\text{O}$	8	8	10	17.9992	0.205

**Table 3. Nuclear Compositions of Atoms of the Very Light Elements**

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
fluorine	${}^{19}_9\text{F}$	9	9	10	18.9984	100
	${}^{20}_{10}\text{Ne}$	10	10	10	19.9924	90.48
neon	${}^{21}_{10}\text{Ne}$	10	10	11	20.9938	0.27
	${}^{22}_{10}\text{Ne}$	10	10	12	21.9914	9.25

[Use this Build an Atom simulator](#) to build atoms of the first 10 elements, see which isotopes exist, check nuclear stability, and gain experience with isotope symbols.

## 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.

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  $^{10}\text{B}$  with a mass of 10.0129 amu, and the remaining 80.1% are  $^{11}\text{B}$  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.

### *Example 2: Calculation of Average Atomic Mass*

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%  $^{20}\text{Ne}$  (mass 19.9924 amu), 0.47%  $^{21}\text{Ne}$  (mass 20.9940 amu), and 7.69%  $^{22}\text{Ne}$  (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

#### **Show Answer**

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924 \text{ amu}) + (0.0047 \times 20.9940 \text{ amu}) + (0.0769 \times 21.9914 \text{ amu}) \\ &= (18.36 + 0.099 + 1.69) \text{ amu} \\ &= 20.15 \text{ amu}\end{aligned}$$

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.)

### *Check Your Learning*

A sample of magnesium is found to contain 78.70% of  $^{24}\text{Mg}$  atoms (mass 23.98 amu), 10.13% of  $^{25}\text{Mg}$  atoms (mass 24.99 amu), and 11.17% of  $^{26}\text{Mg}$  atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Show Answer

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

### *Example 3: Calculation of Percent Abundance*

Naturally occurring chlorine consists of  $^{35}\text{Cl}$  (mass 34.96885 amu) and  $^{37}\text{Cl}$  (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?

Show Answer

The average mass of chlorine is the fraction that is  $^{35}\text{Cl}$  times the mass of  $^{35}\text{Cl}$  plus the fraction that is  $^{37}\text{Cl}$  times the mass of  $^{37}\text{Cl}$ .

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl})$$

If we let  $x$  represent the fraction that is  $^{35}\text{Cl}$ , then the fraction that is  $^{37}\text{Cl}$  is represented by  $1.00 - x$ .

(The fraction that is  $^{35}\text{Cl}$  + the fraction that is  $^{37}\text{Cl}$  must add up to 1, so the fraction of  $^{37}\text{Cl}$  must equal  $1.00 -$  the fraction of  $^{35}\text{Cl}$ .)

Substituting this into the average mass equation, we have:

$$35.453 \text{ amu} = (x \times 34.96885 \text{ amu}) + [(1.00 - x) \times 36.96590 \text{ amu}]$$

$$35.453 = 34.96885x + 36.96590 - 36.96590x$$

$$1.99705x = 1.513$$

$$x = \frac{1.513}{1.99705} = 0.7576$$

So solving yields:  $x = 0.7576$ , which means that  $1.00 - 0.7576 = 0.2424$ . Therefore, chlorine consists of 75.76%  $^{35}\text{Cl}$  and 24.24%  $^{37}\text{Cl}$ .

### *Check Your Learning*

Naturally occurring copper consists of  $^{63}\text{Cu}$  (mass 62.9296 amu) and  $^{65}\text{Cu}$  (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?

Show Answer

69.15% Cu-63 and 30.85% Cu-65

[Visit the PhET Isotopes and Atomic Mass site](#) to 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.

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), 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 than 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.

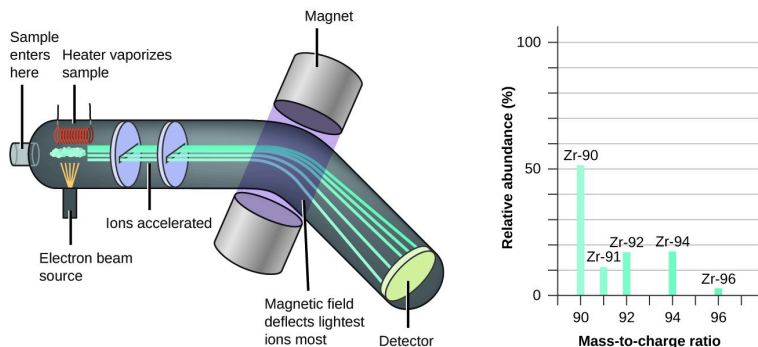


Figure 5. Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

See an animation that explains mass spectrometry.



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<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=42#oembed-1>

Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.



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can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=42#oembed-2>

## *Key Concepts and Summary*

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  $1.6605 \times 10^{-24}$  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. An atom is neutral when it contains equal numbers of electrons and protons.

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. 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. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

### *Key Equations*

- $$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

### *Exercises*

1. In what way are isotopes of a given element always different? In what way(s) are they always the same?
2. Write the symbol for each of the following ions:
  - a. the ion with a 1+ charge, atomic number 55, and mass number 133
  - b. the ion with 54 electrons, 53 protons, and 74

- neutrons
- c. the ion with atomic number 15, mass number 31, and a  $3^-$  charge
  - d. the ion with 24 electrons, 30 neutrons, and a  $3^+$  charge
3. Write the symbol for each of the following ions:
- a. the ion with a  $3^+$  charge, 28 electrons, and a mass number of 71
  - b. the ion with 36 electrons, 35 protons, and 45 neutrons
  - c. the ion with 86 electrons, 142 neutrons, and a  $4^+$  charge
  - d. the ion with a  $2^+$  charge, atomic number 38, and mass number 87
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.

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.
6. Open the [Build an Atom simulation](#)
  - a. Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.
  - b. Now remove one electron to make an ion and give the symbol for the ion you have created.
7. Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:
  - 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).
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 them.
  - a. atomic number 26, mass number 58, charge of 2+
  - b. atomic number 53, mass number 127, charge of 1-
9. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:
  - a.  ${}^{10}_5\text{B}$
  - b.  ${}^{199}_{80}\text{Hg}$
  - c.  ${}^{63}_{29}\text{Cu}$
  - d.  ${}^{13}_6\text{C}$
  - e.  ${}^{77}_{34}\text{Se}$
10. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:
  - a.  ${}^7_3\text{Li}$
  - b.  ${}^{125}_{52}\text{Te}$
  - c.  ${}^{109}_{47}\text{Ag}$
  - d.  ${}^{15}_7\text{N}$
  - e.  ${}^{31}_{15}\text{P}$

11. Click on the [Isotopes and Common Mass website](#) and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron
  - a. Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.
  - b. Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.
  - 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.
12. Repeat Exercise 11 using an element that has three naturally occurring isotopes.
13. 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.

14. Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes  $^{79}\text{Br}$  and  $^{81}\text{Br}$ , 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.
15. 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%  $^6\text{Li}$  and 92.5%  $^7\text{Li}$ , 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%  $^6\text{Li}$  (and the rest  $^7\text{Li}$ ). Calculate the average atomic mass values for each of these two sources.
16. 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 ( $^{10}\text{B}$ , 10.0129 amu and  $^{11}\text{B}$ , 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.
17. The  $^{18}\text{O}$ : $^{16}\text{O}$  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?

Show Selected Answers

2. (a)  $^{133}\text{Cs}^+$ ; (b)  $^{127}\text{I}^-$ ; (c)  $^{31}\text{P}^{3-}$ ; (d)  $^{57}\text{Co}^{3+}$

4. The answers are as follows:

- a. Carbon-12,  $^{12}\text{C}$
- b. This atom contains six protons and six neutrons. There are six electrons in a neutral  $^{12}\text{C}$  atom. The net charge of such a neutral atom is zero, and the mass number is 12.
- c. The preceding answers are correct.
- d. The atom will be stable since C-12 is a stable isotope of carbon.
- e. The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

6. The answers are as follows:

- a. Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is  $^6\text{Li}$  or  $^6_3\text{Li}$
- b.  $^6\text{Li}^+$  or  $^6_3\text{Li}^+$

8. The answers are as follows:

- a. iron, 26 protons, 24 electrons, and 32 neutrons
- b. iodine, 53 protons, 54 electrons, and 74 neutrons

10. The number of protons, electrons, and neutrons for each isotope are as follows:

- a. 3 protons, 3 electrons, 4 neutrons
- b. 52 protons, 52 electrons, 73 neutrons

- c. 47 protons, 47 electrons, 62 neutrons
- d. 7 protons, 7 electrons, 8 neutrons
- e. 15 protons, 15 electrons, 16 neutrons

12. Let us use neon as an example. Since there are three isotopes, 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.

14. 79.904 amu

16. Turkey source: 0.2649 (of 10.0129 amu isotope); US source: 0.2537 (of 10.0129 amu isotope)

## Glossary

**anion:** negatively charged atom or molecule (contains more electrons than protons)

**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  $\frac{1}{12}$  of the mass of a  $^{12}\text{C}$  atom

**atomic number (Z):** number of protons in the nucleus of an atom

**cation:** positively charged atom or molecule (contains fewer electrons than protons)

**chemical symbol:** one-, two-, or three-letter abbreviation used to represent an element or its atoms

**Dalton (Da):** alternative unit equivalent to the atomic mass unit

**fundamental unit of charge:** (also called the elementary charge) equals the magnitude of the charge of an electron (e) with  $e = 1.602 \times 10^{-19} \text{ C}$

**ion:** electrically charged atom or molecule (contains unequal numbers of protons and electrons)

**mass number (A):** sum of the numbers of neutrons and protons in the nucleus of an atom

**unified atomic mass unit (u):** alternative unit equivalent to the atomic mass unit

## 23. Electronic Structure of Atoms

### *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 1 depicts how these two trends in increasing energy relate. The 1s orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2s and then 2p, 3s, and 3p 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. The 3d orbital is higher in energy than the 4s orbital. Such overlaps continue to occur frequently as we move up the chart.

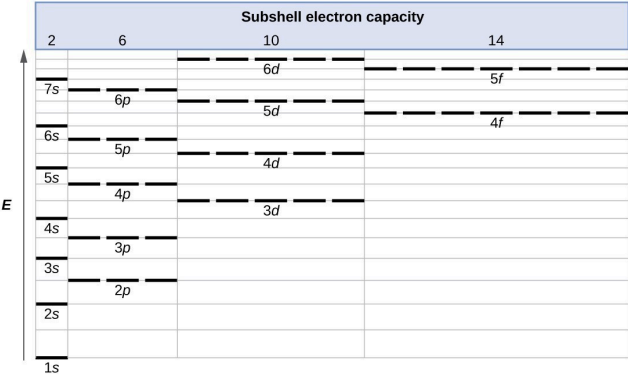


Figure 1. Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

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 5p orbitals fill immediately after the 4d, and immediately before the 6s. 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). 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 and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals ( $1s$  through  $3p$ ), 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 called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 2):

1. The number of the principal quantum 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  $n = 3$ .

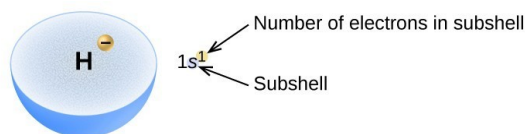


Figure 2. The diagram of an electron configuration specifies the subshell ( $n$  and  $l$  value, with letter symbol) and superscript number of electrons.

# The Aufbau Principle

To determine the electron configuration 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 1), 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 3 illustrates the traditional way to remember the filling order for atomic orbitals. Since the arrangement of the periodic table is based on the electron configurations, Figure 4 provides an alternative 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  $3p$  block up to Ar, we see the orbital will be  $4s$  (K, Ca), followed by the  $3d$  orbitals.

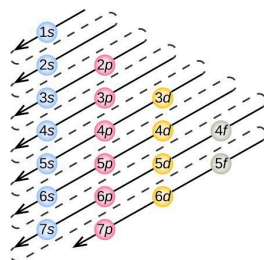


Figure 3. The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the  $s$  orbitals with each  $n$  shell on a separate row. Repeat for  $p$ ,  $d$ , and  $f$ . Be sure to only include orbitals allowed by the quantum numbers (no  $1p$  or  $2d$ , and so forth). Finally, draw diagonal lines from top to bottom as shown.



**Electron Configuration Table**

**Period** (vertical axis): 1, 2, 3, 4, 5, 6, 7

**Group** (horizontal axis): 1, 2, 13, 14, 15, 16, 17, 18

**Electron Configuration for H:**

Name →	<b>H</b>	1 ← Electrons
	<b>1s</b>	← Subshell

Figure 4. 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.

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. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 3 or Figure 4, we would expect to find the electron in the 1s orbital. By convention, the  $m_s = +\frac{1}{2}$  value is usually filled first. The electron configuration and the orbital diagram are:

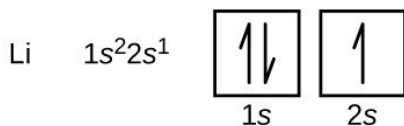


This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

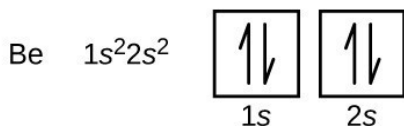


The next atom is the alkali metal lithium with an atomic number

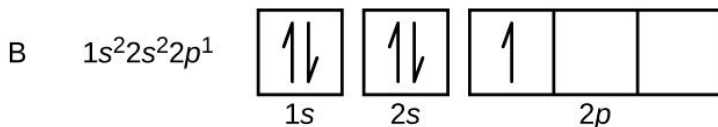
of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital (Figure 3 or Figure 4). Thus, the electron configuration and orbital diagram of lithium are:



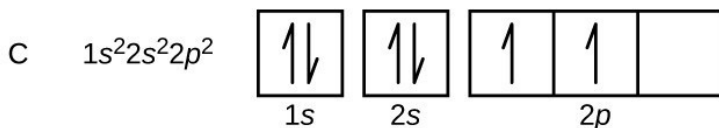
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.



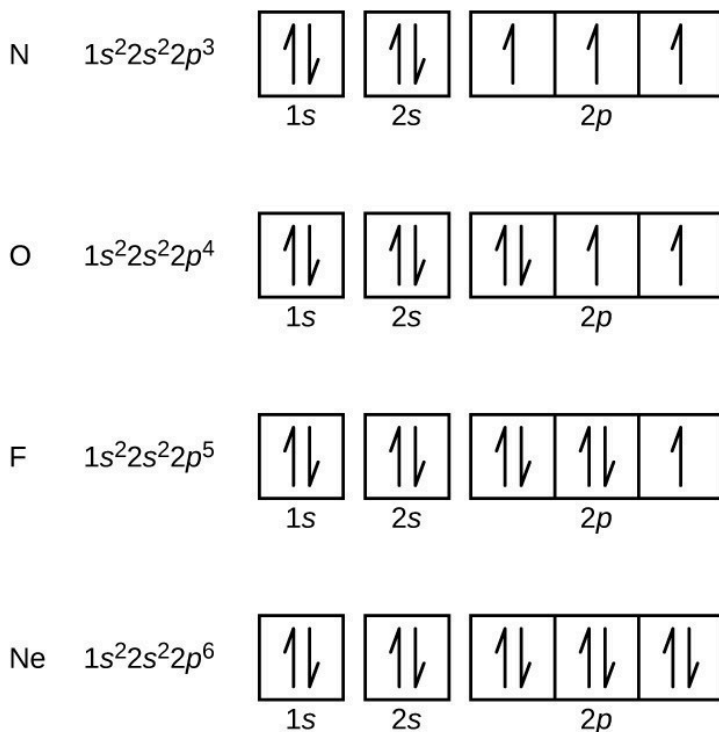
An atom of boron (atomic number 5) contains five electrons. The  $n = 1$  shell is filled with two electrons and three electrons will occupy the  $n = 2$  shell. Because any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2p orbital. There are three degenerate 2p 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.



Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2p subshell. We now have a choice of filling one of the 2p 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 2p 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:



Nitrogen (atomic number 7) fills the 1s and 2s subshells and has one electron in each of the three 2p orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2p orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2p 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:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s 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 5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons,

( $1s^2 2s^2 2p^6$ ) and our abbreviated or condensed configuration is  $[\text{Ne}]3s^1$ .

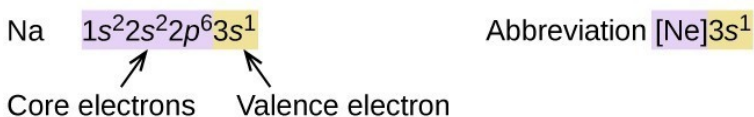


Figure 5. A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as  $[\text{He}]2s^1$ , where  $[\text{He}]$  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.



The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a  $[\text{Ne}]3s^2$  configuration, is analogous to its family member beryllium,  $[\text{He}]2s^2$ . Both atoms have a filled  $s$  subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration  $[\text{Ne}]3s^2 3p^1$ , is analogous to its family member boron,  $[\text{He}]2s^2 2p^1$ .

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 6 shows the lowest energy, or

ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

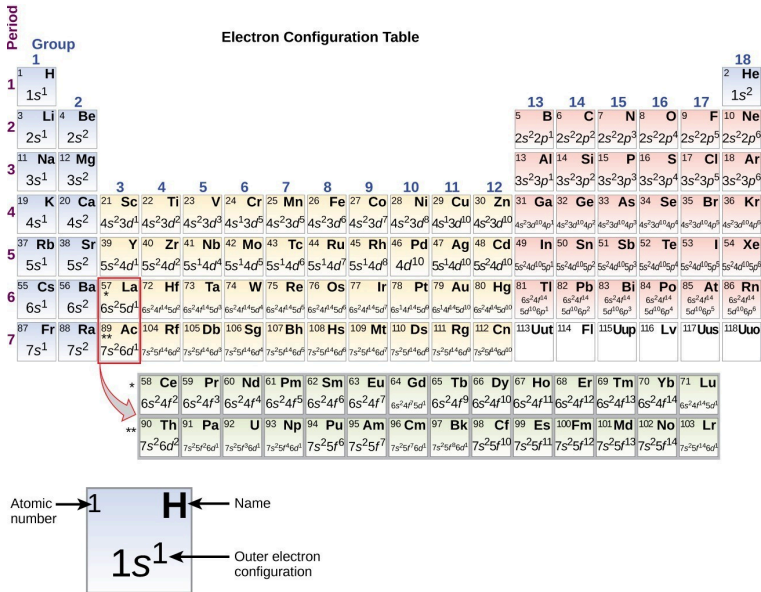


Figure 6. This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3d 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 3d level but is, instead, added to the 4s level (Figure 6). As discussed previously, the 3d orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4s, which has three radial nodes. Thus, potassium has an electron configuration of [Ar]4s<sup>1</sup>. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4s subshell and calcium has

an electron configuration of  $[\text{Ar}]4s^2$ . This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the  $3d$  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  $4p$  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.

### *Example 1: 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?

Show Answer

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ ,  $4s$ , . . . The 15 electrons of the phosphorus atom will fill up to the  $3p$  orbital, which will contain three electrons:





The last electron added is a 3p 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,  $m_s = +\frac{1}{2}$ .

### Check Your Learning

Identify the atoms from the electron configurations given:

1.  $[\text{Ar}]4s^2 3d^5$
2.  $[\text{Kr}]5s^2 4d^{10} 5p^6$

Show Answer

1. Mn
2. Xe

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 3 or Figure 4. For instance, the electron configurations (shown in Figure 6) 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 4s into the 3d orbital to gain the extra stability of a half-filled 3d subshell (in Cr) or a filled 3d subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration  $[\text{Kr}]5s^24d^3$ . Experimentally, we observe that its ground-state electron configuration is actually  $[\text{Kr}]5s^14d^4$ . We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5s orbital are larger than the gap in energy between the 5s and 4d 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.

## 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 6), 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 most 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 behavior 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 6, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 6 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 6. This category includes all the nonmetallic elements, as well as many metals and the intermediate semimetallic 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  $[\text{Ar}]4s^23d^{10}\underline{4p^1}$ , which contains three valence electrons (underlined). 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 6) are not technically transition elements. However, the term is frequently used to refer to the entire  $d$  block (colored yellow in Figure 6), 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 6. 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 atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, 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 a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

## Example 2: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram of:

1.  $\text{Na}^+$
2.  $\text{P}^{3-}$
3.  $\text{Al}^{2+}$
4.  $\text{Fe}^{2+}$
5.  $\text{Sm}^{3+}$

Show Answer

First, write out the electron configuration for each parent atom. We have chosen to show the 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.

1. Na:  $1s^2 2s^2 2p^6 3s^1$ . Sodium cation loses one electron, so  $\text{Na}^+ : 1s^2 2s^2 2p^6 3s^1 = \text{Na}^+ : 1s^2 2s^2 2p^6$ .
2. P:  $1s^2 2s^2 2p^6 3s^2 3p^3$ . Phosphorus trianion gains three electrons, so  $\text{P}^{3-} : 1s^2 2s^2 2p^6 3s^2 3p^6$ .
3. Al:  $1s^2 2s^2 2p^6 3s^2 3p^1$ . Aluminum dication loses two electrons  $\text{Al}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^1 = \text{Al}^{2+} : 1s^2 2s^2 2p^6 3s^1$ .
4. Fe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ . Iron(II) loses two

electrons and, since it is a transition metal, they are removed from the 4s orbital  $\text{Fe}^{2+}$ :

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6.$$

5. Sm:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$ .

Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the 4f orbital.  $\text{Sm}^{3+}$ :

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 =$$

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5.$$

### Check Your Learning

Which ion with a +2 charge has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$ ? Which ion with a +3 charge has this configuration?

Show Answer

$\text{Tc}^{2+}$ ,  $\text{Ru}^{3+}$

### Key Concepts and Summary

The relative energy of the subshells determine the order in which atomic orbitals are filled (1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 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).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior 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).

## *Exercises*

1. Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.
2. Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.
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:

- a. C
  - b. P
  - c. V
  - d. Sb
  - e. Sm
4. Using complete subshell notation ( $1s^2 2s^2 2p^6$ , and so forth), predict the electron configuration of each of the following atoms:
- a. N
  - b. Si
  - c. Fe
  - d. Te
  - e. Tb
5. Is  $1s^2 2s^2 2p^6$  the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.
6. What additional information do we need to answer the question “Which ion has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6$ ?”
7. Draw the orbital diagram for the valence shell of each of the following atoms:
- a. C
  - b. P
  - c. V
  - d. Sb
  - e. Ru
8. Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:



- a. N
  - b. Si
  - c. Fe
  - d. Te
  - e. Mo
9. Using complete subshell notation ( $1s^2 2s^2 2p^6$ , and so forth), predict the electron configurations of the following ions.
- a.  $N^{3-}$
  - b.  $Ca^{2+}$
  - c.  $S^-$
  - d.  $Cs^{2+}$
  - e.  $Cr^{2+}$
  - f.  $Gd^{3+}$
10. Which atom has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$ ?
11. Which atom has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$ ?
12. 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?
13. Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?
14. Which of the following has two unpaired electrons?
- a. Mg
  - b. Si
  - c. S
  - d. Both Mg and S
  - e. Both Si and S.

15. Which atom would be expected to have a half-filled  $6p$  subshell?
16. Which atom would be expected to have a half-filled  $4s$  subshell?
17. 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,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ . Write the electron structure of the two cations.
18. Thallium 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.
19. Write the electron configurations for the following atoms or ions:
- $\text{B}^{3+}$
  - $\text{O}^{-}$
  - $\text{Cl}^{3+}$
  - $\text{Ca}^{2+}$
  - Ti
20. 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.
21. Write a set of quantum numbers for each of the electrons with an  $n$  of 3 in a Sc atom.

Show Selected Answers

2. For example,  $\text{Na}^+ : 1s^2 2s^2 2p^6$ ;  $\text{Ca}^{2+} : 1s^2 2s^2 2p^6$ ;  $\text{Sn}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$ ;  $\text{F}^- : 1s^2 2s^2 2p^6$ ;  $\text{O}^{2-} : 1s^2 2s^2 2p^6$ ;  $\text{Cl}^- : 1s^2 2s^2 2p^6 3s^2 3p^6$ .

4. (a)  $1s^2 2s^2 2p^3$ ;

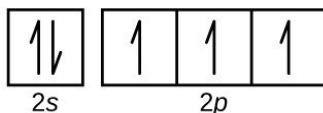
(b)  $1s^2 2s^2 2p^6 3s^2 3p^2$ ;

(c)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ ;

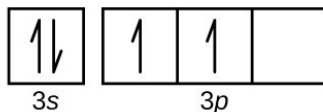
(d)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$ ; (e)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

6. The charge on the ion.

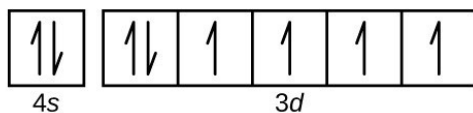
8. (a)



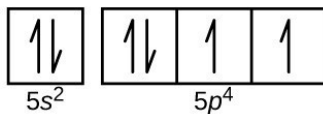
(b)



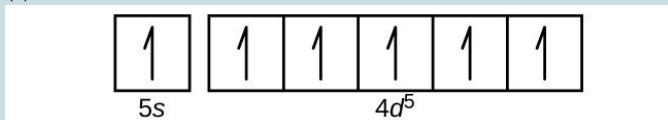
(c)



(d)



(e)



10. Zr

12.  $Rb^+$ ,  $Se^{2-}$

14. Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

16. K

18.  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 4f^{14} 5d^{10}$

20. Co has 27 protons, 27 electrons, and 33 neutrons:  
 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ .

I has 53 protons, 53 electrons, and 78 neutrons:  
 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$ .

## Glossary

**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

**core electron:** electron in an atom that occupies the orbitals of the inner shells

**electron configuration:** electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

**Hund’s rule:** every orbital in a subshell is singly occupied with one

electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

**orbital diagram:** pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

**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

## 24. Elements and The Periodic Table

### *Learning Objectives*

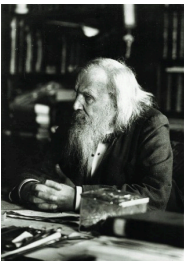
By the end of this section, you will be able to:

- 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

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. 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 1).



(a)

	Gruppe I. — R <sup>0</sup>	Gruppe II. — R <sup>0</sup>	Gruppe III. — R <sup>0</sup> <sup>a</sup>	Gruppe IV. RR <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppe V. RR <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppe VI. RR <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppe VII. RR <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppe VIII. — R <sup>0</sup> <sup>a</sup>
1	Li==1							
2	Li==7	Be==9,4	B==11	C==12	N==14	O==16	F==19	
3	Na==23	Mg==24	Al==27,5	Si==28	P==31	S==32	Cl==35,5	
4	K==39	Ca==40	—==44	Ti==48	V==51	Cr==52	Mn==55	Fe==56, Co==58, Ni==59, Cu==63.
5	(Cu==63)	Zn==65	—==68	—==72	As==75	Se==78	Br==80	
6	Rb==86	Zr==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	Sa==118	Sb==120	Te==125	J==127	
8	Ce==133	Ba==137	Pb==138	Pb==140	—	—	—	—
9	(—)	—	—	—	—	—	—	—
10	—	—	Pb==178	Pb==180	Ta==182	W==184	—	Os==195, Ir==197, Pt==196, Au==199.
11	(Au==199)	Hg==200	Tl==204	Pb==207	Bi==208	—	—	—
12	—	—	—	Th==231	—	U==240	—	—

(b)

Figure 1. (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

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 2). 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.

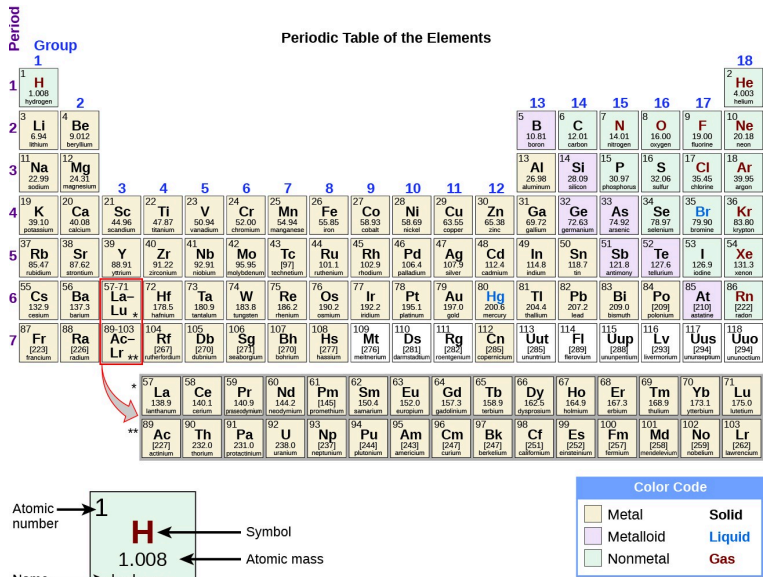


Figure 2. Elements in the periodic table are organized according to their properties.

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. 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).

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). 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.



1. chlorine
2. calcium
3. sodium
4. sulfur

Show Answer

The family names are as follows:

1. halogen
2. alkaline earth metal
3. alkali metal
4. chalcogen

### *Check Your Learning*

Give the group name for each of the following elements:

1. krypton
2. selenium
3. barium
4. lithium

Show Answer

1. noble gas
2. chalcogen
3. alkaline earth metal
4. alkali metal

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.

### *Key Concepts and Summary*

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.

## Exercises

### *Metal or Nonmetal?*

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
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

Show Answer

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 element

### *Identifying Elements*

1. 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
2. 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
3. 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
4. Use the periodic table to give the name and symbol for each of the following elements:
- a. the halogen in the same period as the alkali metal with 11 protons
  - b. the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
  - c. the noble gas in the same row as an isotope with 30 neutrons and 25 protons
  - d. the noble gas in the same period as gold
5. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.
- a. the alkali metal with 11 protons and a mass number of 23
  - b. the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom
  - c. the isotope with 33 protons and 40 neutrons in its nucleus
  - d. the alkaline earth metal with 88 electrons and 138 neutrons
6. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass

number for each.

- a. the chalcogen with a mass number of 125
- b. the halogen whose longest-lived isotope is radioactive
- c. the noble gas, used in lighting, with 10 electrons and 10 neutrons
- d. the lightest alkali metal with three neutrons

Show Selected Answers

1. (a) He; (b) Be; (c) Li; (d) O
3. (a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te
5. (a)  ${}_{11}^{23}\text{Na}$ ; (b)  ${}_{54}^{129}\text{Xe}$ ; (c)  ${}_{33}^{73}\text{As}$ ; (d)  ${}_{88}^{226}\text{Ra}$

## Glossary

**actinide:** inner transition metal in the bottom of the bottom two rows of the periodic table

**alkali metal:** element in group 1

**alkaline earth metal:** element in group 2

**chalcogen:** element in group 16

**group:** vertical column of the periodic table

**halogen:** element in group 17

**inert gas:** (also, noble gas) element in group 18

**inner transition metal:** (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, if in the second row, also called actinide

**lanthanide:** inner transition metal in the top of the bottom two rows of the periodic table



**main-group element:** (also, representative element) element in columns 1, 2, and 12–18

**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

**noble gas:** (also, inert gas) element in group 18

**nonmetal:** element that appears dull, poor conductor of heat and electricity

**period:** (also, series) horizontal row of the period 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

**pnictogen:** element in group 15

**representative element:** (also, main-group element) element in columns 1, 2, and 12–18

**series:** (also, period) horizontal row of the period table

**transition metal:** element in columns 3–11

## 25. Periodic Variations in Element Properties

### *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 behavior. 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 colorless 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 behavior. 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.

Explore [visualizations of the periodic trends discussed in this section \(and many more trends\) on the Atomic Number of the Elements website](#). 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.

## 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 1), 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 1 and Figure 1. The trends for the entire periodic table can be seen in Figure 1.

Table 1. 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

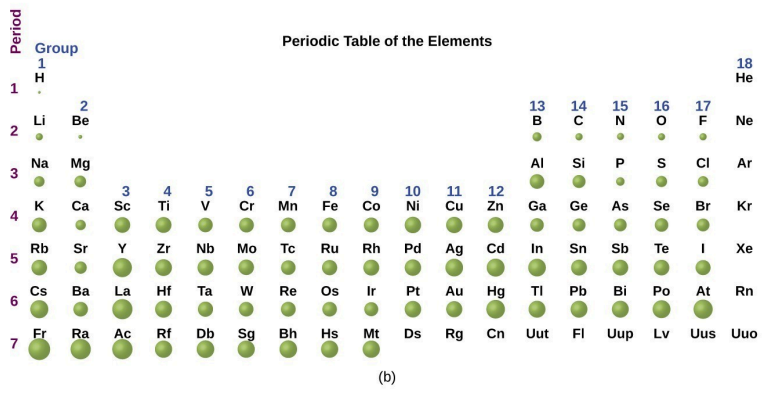
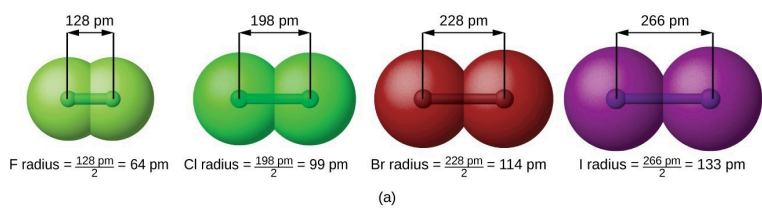


Figure 1. (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as  $n$  increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

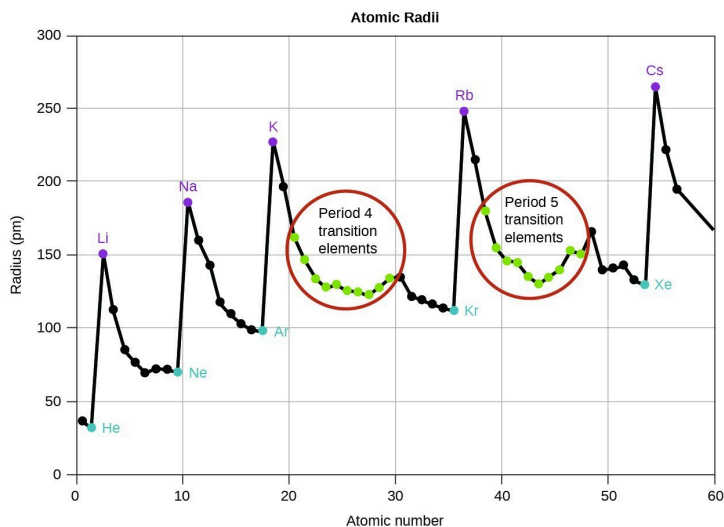


Figure 2. Within each period, the trend in atomic radius decreases as  $Z$  increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as  $Z$  increases.

As shown in Figure 2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. 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,  $Z_{\text{eff}}$** . 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 ( $Z_{\text{eff}}$ ) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{shielding}$$

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,  $Z_{\text{eff}}$  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 1: Sorting Atomic Radii*

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Show Answer

Radius increases as we move down a group, so  $\text{Ge} < \text{Fl}$  (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so  $\text{Kr} < \text{Br} < \text{Ge}$ . Putting the trends together, we obtain  $\text{Kr} < \text{Br} < \text{Ge} < \text{Fl}$ .

### Check Your Learning

Give an example of an atom whose size is smaller than fluorine.

Show Answer

Ne or He

## 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 3). For example, the covalent radius of an aluminum atom ( $1s^2 2s^2 2p^6 3s^2 3p^1$ ) is 118 pm, whereas the ionic radius of an  $\text{Al}^{3+}$  ( $1s^2 2s^2 2p^6$ ) 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  $Z_{\text{eff}}$  (as discussed) and are drawn even closer to the nucleus.



Figure 3. 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

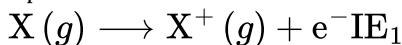
charges (e.g.,  $V^{2+}$  has an ionic radius of 79 pm, while that of  $V^{3+}$  is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number,  $n$ .

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  $Z_{\text{eff}}$  per electron. Both effects (the increased number of electrons and the decreased  $Z_{\text{eff}}$ ) cause the radius of an anion to be larger than that of the parent atom (Figure 3). For example, a sulfur atom ( $[\text{Ne}]3s^23p^4$ ) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ( $[\text{Ne}]3s^23p^6$ ) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

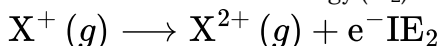
Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are  $N^{3-}$ ,  $O^{2-}$ ,  $F^-$ , Ne,  $Na^+$ ,  $Mg^{2+}$ , and  $Al^{3+}$  ( $1s^22s^22p^6$ ). Another isoelectronic series is  $P^{3-}$ ,  $S^{2-}$ ,  $Cl^-$ , Ar,  $K^+$ ,  $Ca^{2+}$ , and  $Sc^{3+}$  ( $[\text{Ne}]3s^23p^6$ ). 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.

## 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:



The energy required to remove the second most loosely bound electron is called the second ionization energy ( $IE_2$ ).





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.

Figure 4 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 5. 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 in this chapter). 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 ( $[\text{He}]2s^2$ ) is an  $s$  electron, whereas the electron removed during the ionization of boron ( $[\text{He}]2s^22p^1$ ) 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.

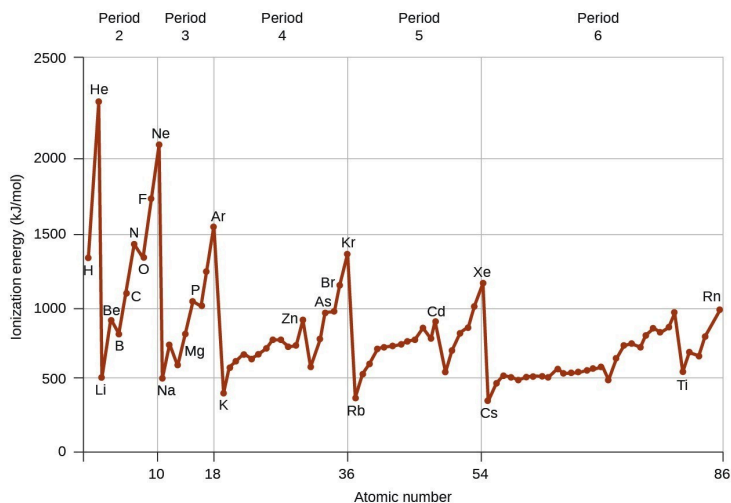


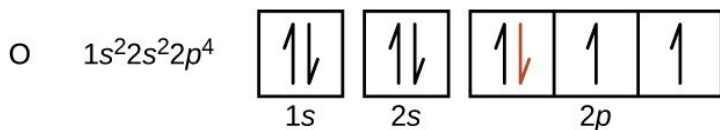
Figure 4. The first ionization energy of the elements in the first five periods are plotted against their atomic number.

Period		First Ionization Energies of Some Elements (kJ/mol)																18		
Group																				
1	2													13	14	15	16	17	18	
1	H 1310													B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080	
2	Li 520	Be 900													Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
3	Na 490	Mg 730	3	4	5	6	7	8	9	10	11	12	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350		
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 5. This version of the periodic table shows the first ionization energy of (IE<sub>1</sub>), in kJ/mol, of selected elements.

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  $2p$  orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 5).



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 2, there is a large increase in the ionization energies (color 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 2. Successive Ionization Energies for Selected Elements (kJ/mol)**

Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>
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	N/A	N/A
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	N/A

### *Example 2: Ranking Ionization Energies*

Predict the order of increasing energy for the following processes: IE<sub>1</sub> for Al, IE<sub>1</sub> for Tl, IE<sub>2</sub> for Na, IE<sub>3</sub> for Al.

Show Answer

Removing the 6p<sup>1</sup> electron from Tl is easier than removing the 3p<sup>1</sup> electron from Al because the higher *n* orbital is farther from the nucleus, so IE<sub>1</sub>(Tl) < IE<sub>1</sub>(Al).

Ionizing the third electron from

Al ( $\text{Al}^{2+} \longrightarrow \text{Al}^{3+} + \text{e}^-$ ) requires more energy because the cation Al<sup>2+</sup> exerts a stronger pull on the electron than the neutral Al atom, so IE<sub>1</sub>(Al) < IE<sub>3</sub>(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<sub>1</sub>(Tl) < IE<sub>1</sub>(Al) < IE<sub>3</sub>(Al) < IE<sub>2</sub>(Na).

### *Check Your Learning*

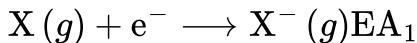
Which has the lowest value for  $IE_1$ : O, Po, Pb, or Ba?

Show Answer

Ba

## 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).



This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. 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.

Period		Electron Affinity Values for Selected Elements (kJ/mol)																		18				
Group																								
1																								
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 -115	Sb -7	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				

\* Calculated value

Figure 6. This version of the periodic table displays the electron affinity values (in in kJ/mol) for selected elements.

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 favorable 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 in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

## Key Concepts and Summary

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 favorable (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.

## *Exercises*

1. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.
2. Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.



3. Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.
4. Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.
5. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb
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
7. Atoms of which group in the periodic table have a valence shell electron configuration of  $ns^2np^3$ ?
8. Atoms of which group in the periodic table have a valence shell electron configuration of  $ns^2$ ?
9. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.
10. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.
11. Based on their positions in the periodic table, list the following ions in order of increasing radius:  $K^+$ ,  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Si^{4+}$ .
12. List the following ions in order of increasing radius:  $Li^+$ ,  $Mg^{2+}$ ,  $Br^-$ ,  $Te^{2-}$ .
13. Which atom and/or ion is (are) isoelectronic with  $Br^+$ :  $Se^{2+}$ , Se,  $As^-$ , Kr,  $Ga^{3+}$ ,  $Cl^-$ ?
14. Which of the following atoms and ions is (are) isoelectronic with  $S^{2+}$ :  $Si^{4+}$ ,  $Cl^{3+}$ , Ar,  $As^{3+}$ , Si,  $Al^{3+}$ ?
15. Compare both the numbers of protons and

electrons present in each to rank the following ions in order of increasing radius:  $\text{As}^{3-}$ ,  $\text{Br}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ .

16. Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.)  
What name is given to the energy for the reaction?  
Hint: note the process depicted does not correspond to electron affinity  $\text{E}^+(g) + e^- \longrightarrow \text{E}(g)$
17. Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.)  
What name is given to the energy for the reaction?  
 $\text{E}(g) \longrightarrow \text{E}^+(g) + e^-$
18. The ionic radii of the ions  $\text{S}^{2-}$ ,  $\text{Cl}^-$ , and  $\text{K}^+$  are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.
19. Which main group atom would be expected to have the lowest second ionization energy?
20. Explain why Al is a member of group 13 rather than group 3?

#### Show Selected Answers

1. Cl
3. O
5.  $\text{Rb} < \text{Li} < \text{N} < \text{F}$
7. 15 (5A)
9.  $\text{Mg} < \text{Ca} < \text{Rb} < \text{Cs}$
11.  $\text{Si}^{4+} < \text{Al}^{3+} < \text{Ca}^{2+} < \text{K}^+$
13. Se,  $\text{As}^-$
15.  $\text{Mg}^{2+} < \text{K}^+ < \text{Br}^- < \text{As}^{3-}$
17. O,  $\text{IE}_1$

## Glossary

**covalent radius:** one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

**effective nuclear charge:** charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

**electron affinity:** energy required to add an electron to a gaseous atom to form an anion

**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 ( $X^{2+}$ )

**isoelectronic:** group of ions or atoms that have identical electron configurations



PART VI

IONS AND COMPOUNDS



## 26. Chemical Formulas

### *Learning Objectives*

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

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

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 1). 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 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.

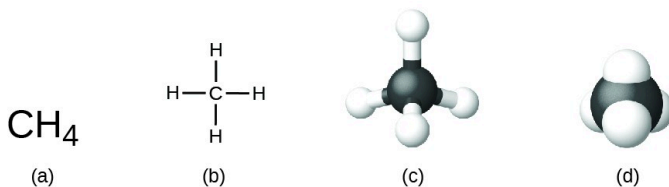


Figure 1. A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

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  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$ , respectively. Other elements commonly found as diatomic molecules are fluorine ( $\text{F}_2$ ), chlorine ( $\text{Cl}_2$ ), bromine ( $\text{Br}_2$ ), and iodine ( $\text{I}_2$ ). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is  $\text{S}_8$  (Figure 2).

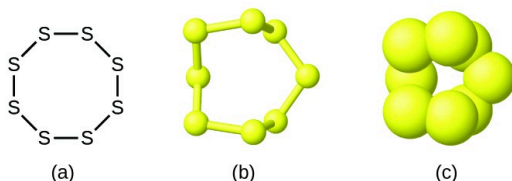


Figure 2. A molecule of sulfur is composed of eight sulfur atoms and is therefore written as  $\text{S}_8$ . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.



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).

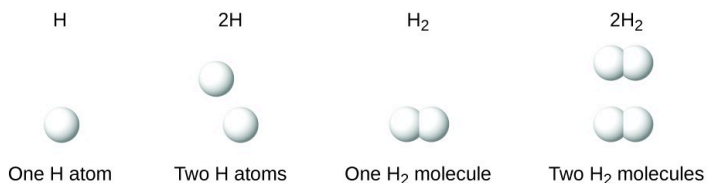


Figure 3. The symbols  $H$ ,  $2H$ ,  $H_2$ , and  $2H_2$  represent very different entities.

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. We sometimes describe the composition of these compounds with an **empirical formula**, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of  $TiO_2$ . This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 4).

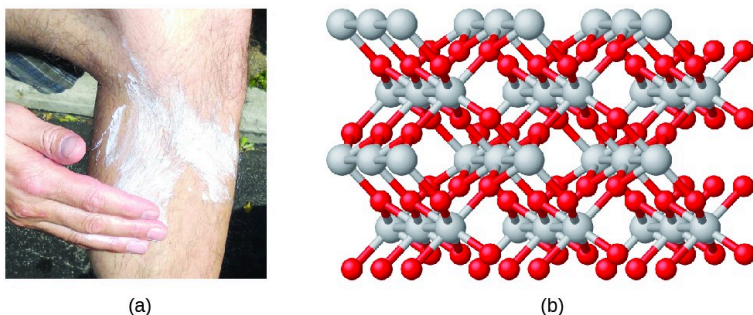


Figure 4. (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide,  $\text{TiO}_2$ , contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr)

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. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its **molecular mass** (the sum of atomic masses for all atoms composing the molecule). 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. Thus, the empirical formula is CH. 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  $\text{C}_6\text{H}_6$  (Figure 5).

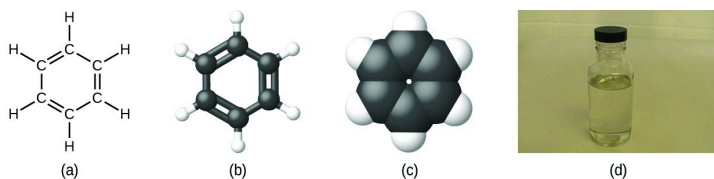


Figure 5. Benzene,  $C_6H_6$ , is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is  $C_2H_4O_2$ . This formula indicates that a molecule of acetic acid (Figure 6) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is  $CH_2O$ . Note that a molecular formula is always a whole-number multiple of an empirical formula.

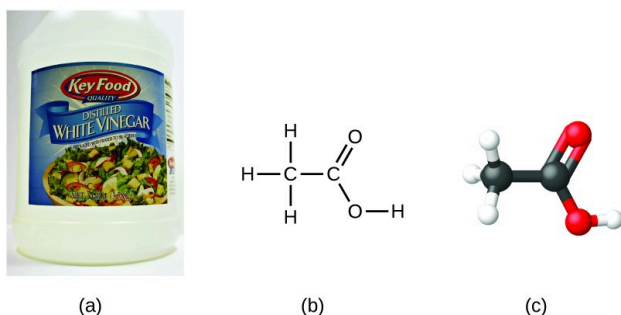


Figure 6. (a) Vinegar contains acetic acid,  $C_2H_4O_2$ , which has an empirical formula of  $CH_2O$ . It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

### *Example 1: Empirical and Molecular Formulas*

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

Show Answer

The molecular formula is  $\text{C}_6\text{H}_{12}\text{O}_6$  because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is  $\text{CH}_2\text{O}$ .

### *Check Your Learning*

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

Show Answer

Molecular formula,  $\text{C}_8\text{H}_{16}\text{O}_4$ ; empirical formula,  $\text{C}_2\text{H}_4\text{O}$

You can explore [PhET's molecule building](#) using an online simulation.

## Portrait of a Chemist: Lee Cronin

What is it that chemists do?

According to Lee **Cronin** (Figure 7), chemists make very complicated molecules by “chopping up” small molecules and “reverse engineering” them. He wonders if we could “make a really cool universal chemistry set” by what he calls “app-ing” chemistry. Could we “app” chemistry?



*Figure 7. Chemist Lee Cronin has been named one of the UK's 10 most inspirational scientists. (credit: image courtesy of Lee Cronin)*

In a 2012 TED talk, Lee describes one fascinating possibility: combining a collection of chemical “inks” with a 3D printer capable of fabricating a reaction apparatus (tiny test tubes, beakers, and the like) to fashion a “universal toolkit of chemistry.” This toolkit could be used to create custom-tailored drugs to fight a new superbug or to “print” medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, “What Apple did for music, I’d like to do for the discovery and

distribution of prescription drugs.”<sup>1</sup> View his full talk from the TED website.



One or more interactive elements has been excluded from this version of the text. You can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=47#oembed-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. For example, could there be another compound with the same formula as acetic acid,  $C_2H_4O_2$ ? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula  $C_2H_4O_2$  could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be

1. Lee Cronin, “Print Your Own Medicine,” Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.

arranged to form a methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of **isomers**—compounds with the same chemical formula but different molecular structures (Figure 8). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.

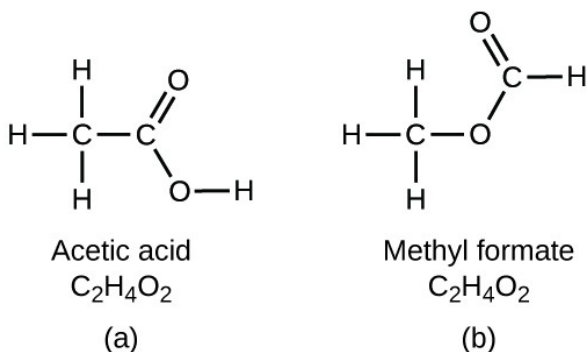


Figure 8. Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ( $C_2H_4O_2$ ) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 9). Acetic acid and methyl formate are **structural isomers**, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of **spatial isomers**, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. S-(+)-carvone smells like caraway, and R-(-)-carvone smells like spearmint.

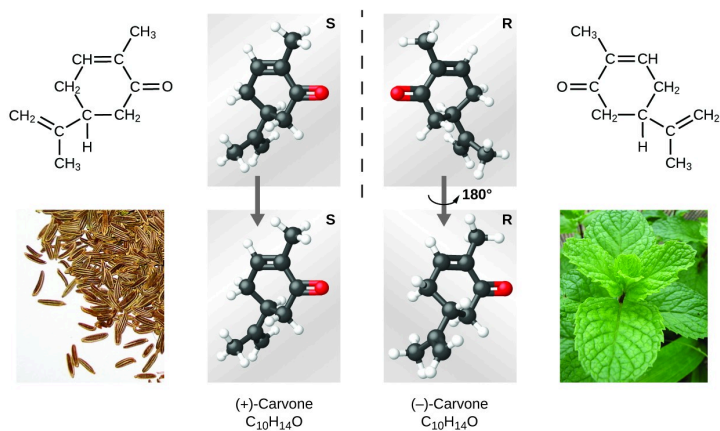


Figure 9. Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by “Miansari66”/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

## Key Concepts and Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.



## Exercises

1. Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.
2. Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.
3. Write the molecular and empirical formulas of the following compounds:

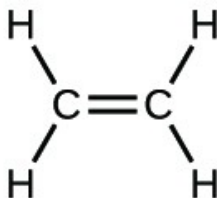
a.



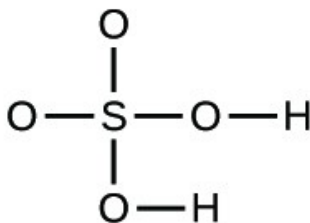
b.



c.

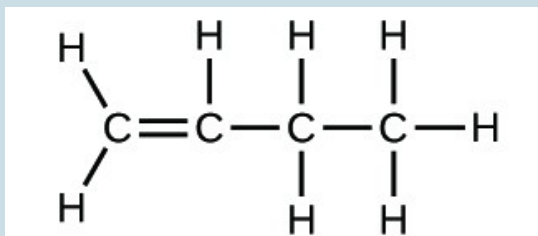


d.

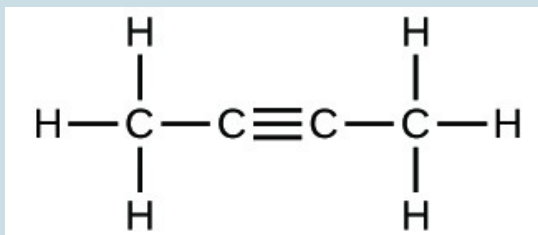


4. Write the molecular and empirical formulas of the following compounds:

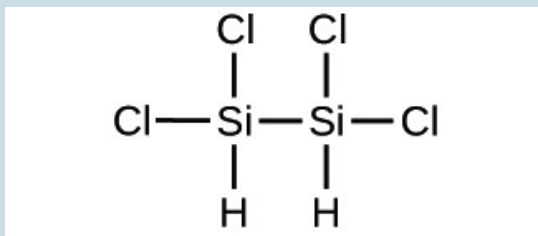
a.



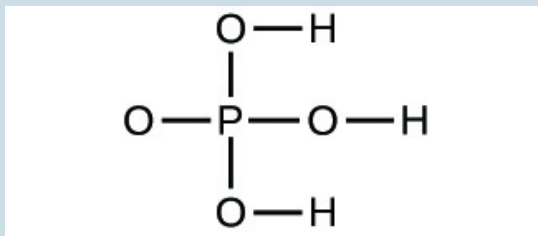
b.



c.



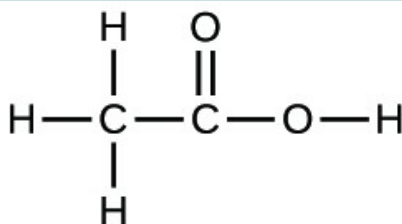
d.



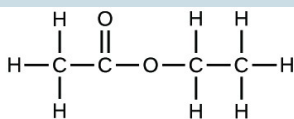
5. Determine the empirical formulas for the following compounds:

- caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
- fructose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

- c. hydrogen peroxide,  $\text{H}_2\text{O}_2$
  - d. glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$
  - e. ascorbic acid (vitamin C),  $\text{C}_6\text{H}_8\text{O}_6$
6. Determine the empirical formulas for the following compounds:
- a. acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$
  - b. citric acid,  $\text{C}_6\text{H}_8\text{O}_7$
  - c. hydrazine,  $\text{N}_2\text{H}_4$
  - d. nicotine,  $\text{C}_{10}\text{H}_{14}\text{N}_2$
  - e. butane,  $\text{C}_4\text{H}_{10}$
7. Write the empirical formulas for the following compounds:



a.



b.

#### Show Selected Answers

1. The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen,  $\text{O}_2$ , contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

3. (a) molecular  $\text{CO}_2$ , empirical  $\text{CO}_2$ ; (b) molecular  $\text{C}_2\text{H}_2$ ,

empirical CH; (c) molecular  $C_2H_4$ , empirical  $CH_2$ ; (d) molecular  $H_2SO_4$ , empirical  $H_2SO_4$

5. (a)  $C_4H_5N_2O$ ; (b)  $C_{12}H_{22}O_{11}$ ; (c) HO; (d)  $CH_2O$ ; (e)  $C_3H_4O_3$

7. (a)  $CH_2O$ ; (b)  $C_2H_4O$

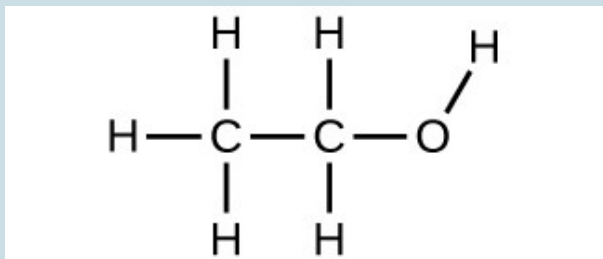
## *PhET Exercises*

1. Open the [Build a Molecule simulation](#) and select the “Larger Molecules” tab. Select an appropriate atoms “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.
  1. Draw the structural formula of this molecule and state its name.
  2. Can you arrange these atoms in any way to make a different compound?
2. Use the [Build a Molecule simulation](#) to repeat question 8, but build a molecule with two carbons, six hydrogens, and one oxygen.
  1. Draw the structural formula of this molecule

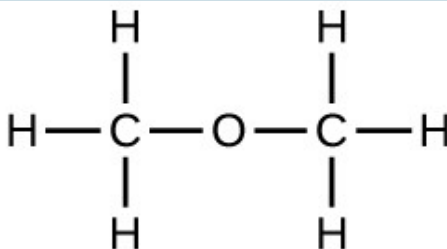
- and state its name.
2. Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
  3. How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).
3. Use the [Build a Molecule simulation](#) to repeat question 8, but build a molecule with three carbons, seven hydrogens, and one chlorine.
- a. Draw the structural formula of this molecule and state its name.
  - b. Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
  - c. How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

Show Answers to Question 2

- a. ethanol



- b. methoxymethane, more commonly known as dimethyl ether



- c. These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

## Glossary

**empirical formula:** formula showing the composition of a compound given as the simplest whole-number ratio of atoms

**isomers:** compounds with the same chemical formula but different structures

**molecular formula:** formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

**spatial isomers:** compounds in which the relative orientations of the atoms in space differ

**structural formula:** shows the atoms in a molecule and how they are connected

# 27. Molecular and Ionic Compounds

## *Learning Objectives*

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

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic 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 1).

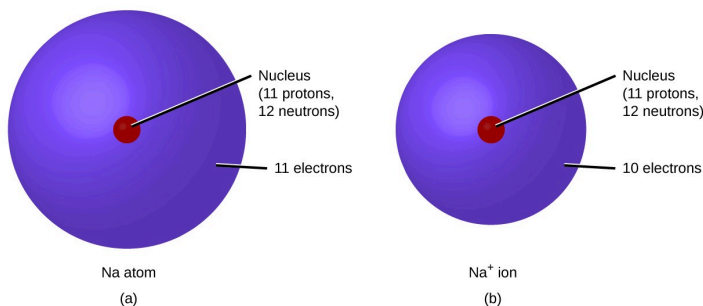


Figure 1. (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na<sup>+</sup>) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

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<sup>+</sup> charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2<sup>+</sup> 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<sup>+</sup> charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca<sup>2+</sup>. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca<sup>2+</sup> 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<sup>-</sup> charge; atoms of group 16 gain two electrons and form ions with a 2<sup>-</sup> 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<sup>-</sup> charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br<sup>-</sup>. (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 of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 2). 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<sup>+</sup> ions; group 2 elements form 2<sup>+</sup> 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<sup>-</sup> ions; group 16 elements (two groups left) form 2<sup>-</sup> 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<sup>+</sup> or 2<sup>+</sup> charge, and iron can form ions with a 2<sup>+</sup> or 3<sup>+</sup> charge.

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																			He
2		Li <sup>+</sup>	Be <sup>2+</sup>												C <sup>4-</sup>	N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	Ne
3		Na <sup>+</sup>	Mg <sup>2+</sup>											Al <sup>3+</sup>		P <sup>3-</sup>	S <sup>2-</sup>	Cl <sup>-</sup>	Ar
4		K <sup>+</sup>	Ca <sup>2+</sup>				Cr <sup>3+</sup> Cr <sup>6+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup> Fe <sup>3+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>+</sup> Cu <sup>2+</sup>	Zn <sup>2+</sup>			As <sup>3-</sup>	Se <sup>2-</sup>	Br <sup>-</sup>	Kr
5		Rb <sup>+</sup>	Sr <sup>2+</sup>									Ag <sup>+</sup>	Cd <sup>2+</sup>				Te <sup>2-</sup>	I <sup>-</sup>	Xe
6		Cs <sup>+</sup>	Ba <sup>2+</sup>								Pt <sup>2+</sup>	Au <sup>+</sup> Au <sup>3+</sup>	Hg <sub>2</sub> <sup>2+</sup> Hg <sub>2</sub> <sup>+</sup>					At <sup>-</sup>	Rn
7		Fr <sup>+</sup>	Ra <sup>2+</sup>																

*Note: In the original figure, the elements from Group 1 to 2 and Period 6 to 7 are highlighted in green. A red box highlights the elements from Group 1 to 2 and Period 6 to 7. A red arrow points from the red box to the elements in the green box.*

Figure 2. Some elements exhibit a regular pattern of ionic charge when they form ions.

### *Example 1: Composition of Ions*

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Show Answer

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,  $\text{Al}^{3+}$ .

### *Check Your Learning*

Give the symbol and name for the ion with 34 protons and 36 electrons.

Show Answer

$\text{Se}^{2-}$ , the selenide ion

### *Example 2: 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.

Show Answer

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  $\text{Mg}^{2+}$ , 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  $\text{N}^{3-}$ , and it is called a nitride ion.

### *Check Your Learning*

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.

Show Answer

Al will form a cation with a charge of  $3+$ :  $\text{Al}^{3+}$ , an aluminum ion. Carbon will form an anion with a charge of  $4-$ :  $\text{C}^{4-}$ , a carbide ion.

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 1. **Oxyanions** are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

**Table 1. Common Polyatomic Ions**

Charge	Name	Formula	Charge	Name	Formula
1+	ammonium	$\text{NH}_4^+$	1-	permanganate	$\text{MnO}_4^-$
1-	acetate	$\text{C}_2\text{H}_3\text{O}_2^-$	1-	hydrogen carbonate, or bicarbonate	$\text{HCO}_3^-$
1-	cyanide	$\text{CN}^-$	2-	carbonate	$\text{CO}_3^{2-}$
1-	hydroxide	$\text{OH}^-$	2-	peroxide	$\text{O}_2^{2-}$
1-	nitrate	$\text{NO}_3^-$	1-	hydrogen sulfate, or bisulfate	$\text{HSO}_4^-$
1-	nitrite	$\text{NO}_2^-$	2-	sulfate	$\text{SO}_4^{2-}$
1-	perchlorate	$\text{ClO}_4^-$	2-	sulfite	$\text{SO}_3^{2-}$
1-	chlorate	$\text{ClO}_3^-$	1-	dihydrogen phosphate	$\text{H}_2\text{PO}_4^-$
1-	chlorite	$\text{ClO}_2^-$	2-	hydrogen phosphate	$\text{HPO}_4^{2-}$
1-	hypochlorite	$\text{ClO}^-$	3-	phosphate	$\text{PO}_4^{3-}$

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  $\text{ClO}_4^-$ , chlorate is  $\text{ClO}_3^-$ , chlorite is  $\text{ClO}_2^-$  and hypochlorite is  $\text{ClO}^-$ . Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is  $\text{NO}_3^-$  while sulfate is  $\text{SO}_4^{2-}$ . This will be covered in more detail in the next module on nomenclature.

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.

## 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,  $\text{Na}^+$ , and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion,  $\text{Cl}^-$ , the resulting compound,  $\text{NaCl}$ , is composed of sodium ions and chloride ions in the ratio of one  $\text{Na}^+$  ion for each  $\text{Cl}^-$  ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form  $\text{CaCl}_2$ , which

is composed of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions in the ratio of one  $\text{Ca}^{2+}$  ion to two  $\text{Cl}^-$  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,  $\text{AlCl}_3$ , 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  $801\text{ }^\circ\text{C}$  and boils at  $1413\text{ }^\circ\text{C}$ . (As a comparison, the molecular compound water melts at  $0\text{ }^\circ\text{C}$  and boils at  $100\text{ }^\circ\text{C}$ .) 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 3).

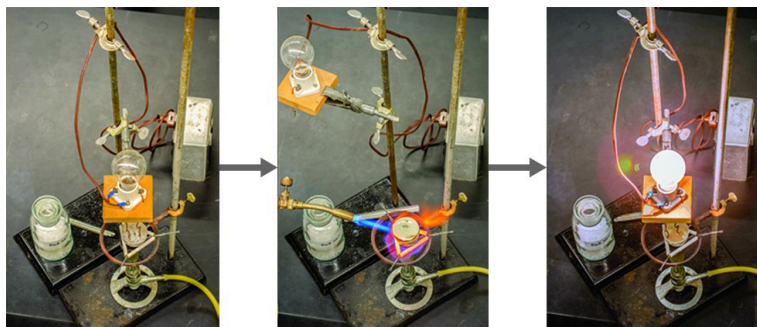


Figure 3. Sodium chloride melts at  $801\text{ }^\circ\text{C}$  and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Watch this video to see a mixture of salts melt and conduct electricity.



One or more interactive elements has been excluded from this version of the text. You can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=48#oembed-1>

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 3: Predicting the Formula of an Ionic Compound*

The gemstone sapphire (Figure 4) is mostly a compound of aluminum and oxygen that contains aluminum cations,  $\text{Al}^{3+}$ , and oxygen anions,  $\text{O}^{2-}$ . What is the formula of this compound?



Figure 4. Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Show Answer

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  $\text{Al}_2\text{O}_3$ .

### *Check Your Learning*

Predict the formula of the ionic compound formed between the sodium cation,  $\text{Na}^+$ , and the sulfide anion,  $\text{S}^{2-}$ .

Show Answer





Many ionic compounds contain polyatomic ions (Table 1) 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  $\text{Ca}_3(\text{PO}_4)_2$ . This formula indicates that there are three calcium ions ( $\text{Ca}^{2+}$ ) for every two phosphate ( $\text{PO}_4^{3-}$ ) groups. The  $\text{PO}_4^{3-}$  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 4: Predicting the Formula of a Compound with a Polyatomic Anion*

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$ . What is the formula of this compound?

Show Answer

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  $\text{Ca}^{2+}$  ion to two  $\text{H}_2\text{PO}_4^-$  ions. We designate this by enclosing the

formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

### *Check Your Learning*

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion,  $\text{O}_2^{2-}$  (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Show Answer

$\text{Li}_2\text{O}_2$

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 cations. For compounds containing only monatomic ions (such as  $\text{NaCl}$ ) and for many compounds containing polyatomic ions (such as  $\text{CaSO}_4$ ), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of  $\text{Na}^+$  and  $\text{C}_2\text{O}_4^{2-}$  ions combined in a 2:1 ratio, and its formula is written as  $\text{Na}_2\text{C}_2\text{O}_4$ . The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula,  $\text{NaCO}_2$ . This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion,  $\text{C}_2\text{O}_4^{2-}$ .

## 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. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

### *Example 5: Predicting the Type of Bonding in Compounds*

Predict whether the following compounds are ionic or molecular:

1. KI, the compound used as a source of iodine in table salt

2.  $\text{H}_2\text{O}_2$ , the bleach and disinfectant hydrogen peroxide
3.  $\text{CHCl}_3$ , the anesthetic chloroform
4.  $\text{Li}_2\text{CO}_3$ , a source of lithium in antidepressants

Show Answer

1. Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
2. Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal;  $\text{H}_2\text{O}_2$  is predicted to be molecular.
3. Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal;  $\text{CHCl}_3$  is predicted to be molecular.
4. Lithium (group 1A) is a metal, and carbonate is a polyatomic ion;  $\text{Li}_2\text{CO}_3$  is predicted to be ionic.

### *Check Your Learning*

Using the periodic table, predict whether the following compounds are ionic or covalent:

1.  $\text{SO}_2$
2.  $\text{CaF}_2$
3.  $\text{N}_2\text{H}_4$
4.  $\text{Al}_2(\text{SO}_4)_3$

Show Answer

1. molecular
2. ionic

3. molecular
4. ionic

### *Key Concepts and Summary*

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. By 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 charge ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

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.

## Exercises

- Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl,  $\text{NCl}_3$ , ICl,  $\text{MgCl}_2$ ,  $\text{PCl}_5$ , and  $\text{CCl}_4$ .
- Using the periodic table, predict whether the following chlorides are ionic or covalent:  $\text{SiCl}_4$ ,  $\text{PCl}_3$ ,  $\text{CaCl}_2$ , CsCl,  $\text{CuCl}_2$ , and  $\text{CrCl}_3$ .
- For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:
  - $\text{NF}_3$
  - BaO,
  - $(\text{NH}_4)_2\text{CO}_3$
  - $\text{Sr}(\text{H}_2\text{PO}_4)_2$
  - IBr
  - $\text{Na}_2\text{O}$
- 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:
  - $\text{KClO}_4$
  - $\text{MgC}_2\text{H}_3\text{O}_2$
  - $\text{H}_2\text{S}$
  - $\text{Ag}_2\text{S}$
  - $\text{N}_2\text{Cl}_4$
  - $\text{Co}(\text{NO}_3)_2$
- For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

- a.  $\text{Ca}^{2+}$ ,  $\text{S}^{2-}$
- b.  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$
- c.  $\text{Al}^{3+}$ ,  $\text{Br}^-$  (d)  $\text{Na}^+$ ,  $\text{HPO}_4^{2-}$  (e)  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$

6. For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

- a.  $\text{K}^+$ ,  $\text{O}^{2-}$
- b.  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$
- c.  $\text{Al}^{3+}$ ,  $\text{O}^{2-}$
- d.  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$
- e.  $\text{Ba}^{2+}$ ,  $\text{PO}_4^{3-}$

Show Selected Answers

1. Ionic:  $\text{KCl}$ ,  $\text{MgCl}_2$ ; Covalent:  $\text{NCl}_3$ ,  $\text{ICl}$ ,  $\text{PCl}_5$ ,  $\text{CCl}_4$

3. (a) covalent; (b) ionic,  $\text{Ba}^{2+}$ ,  $\text{O}^{2-}$ ; (c) ionic,  $\text{NH}_4^+$ ,  $\text{CO}_3^{2-}$ ; (d) ionic,  $\text{Sr}^{2+}$ ,  $\text{H}_2\text{PO}_4^-$ ; (e) covalent; (f) ionic,  $\text{Na}^+$ ,  $\text{O}^{2-}$

5. (a)  $\text{CaS}$ ; (b)  $(\text{NH}_4)_2\text{SO}_4$ ; (c)  $\text{AlBr}_3$ ; (d)  $\text{Na}_2\text{HPO}_4$ ; (e)  $\text{Mg}_3(\text{PO}_4)_2$

## Glossary

**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

**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

**molecular compound:** (also, covalent compound) composed of molecules formed by atoms of two or more different elements

**monatomic ion:** ion composed of a single atom

**oxyanion:** polyatomic anion composed of a central atom bonded to oxygen atoms

**polyatomic ion:** ion composed of more than one atom



## 28. Chemical Nomenclature

### *Learning Objectives*

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

- Derive names for common types of inorganic compounds using a systematic approach

**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  $\text{NaCl}$ ,  $\text{CaCO}_3$ , and  $\text{N}_2\text{O}_4$ . 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 principle element, will be treated in a later chapter on organic chemistry.

### Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular?

If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

## Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *-ide*). Some examples are given in Table 1.

---

**Table 1. Names of Some Ionic Compounds**

NaCl, sodium chloride	Na <sub>2</sub> O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI <sub>2</sub> , calcium iodide	Mg <sub>3</sub> N <sub>2</sub> , magnesium nitride
CsF, cesium fluoride	Ca <sub>3</sub> P <sub>2</sub> , calcium phosphide
LiCl, lithium chloride	Al <sub>4</sub> C <sub>3</sub> , aluminum carbide

---

## Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *-ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table 2.

---

**Table 2. Names of Some Polyatomic Ionic Compounds**

---

KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> , potassium acetate	(NH <sub>4</sub> )Cl, ammonium chloride
NaHCO <sub>3</sub> , sodium bicarbonate	CaSO <sub>4</sub> , calcium sulfate
Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> , aluminum carbonate	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , magnesium phosphate

---

## Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 3. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

---

**Table 3. Everyday Ionic Compounds**

<b>Ionic Compound</b>	<b>Use</b>
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
NaHCO <sub>3</sub> , sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na <sub>2</sub> CO <sub>3</sub> , sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
CaCO <sub>3</sub> calcium carbonate	ingredient in antacids
Mg(OH) <sub>2</sub> , magnesium hydroxide	ingredient in antacids
Al(OH) <sub>3</sub> , aluminum hydroxide	ingredient in antacids
NaOH, sodium hydroxide	lye; used as drain cleaner
K <sub>3</sub> PO <sub>4</sub> , potassium phosphate	food additive (many purposes)
MgSO <sub>4</sub> , magnesium sulfate	added to purified water
Na <sub>2</sub> HPO <sub>4</sub> , sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na <sub>2</sub> SO <sub>3</sub> , sodium sulfite	preservative

---

## Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. 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+ (see [Molecular and Ionic Compounds](#)), and the two corresponding compound formulas are  $\text{FeCl}_2$  and  $\text{FeCl}_3$ . 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 4.

**Table 4. Names of Some Transition Metal Ionic Compounds**

Transition Metal Ionic Compound	Name
$\text{FeCl}_3$	iron(III) chloride
$\text{Hg}_2\text{O}$	mercury(I) oxide
$\text{HgO}$	mercury(II) oxide
$\text{Cu}_3(\text{PO}_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *-ic* and *-ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride,  $\text{FeCl}_3$ , was previously called ferric chloride, and iron(II) chloride,  $\text{FeCl}_2$ , 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  $\text{SnF}_2$ , which is more

properly named tin(II) fluoride. The other fluoride of tin is  $\text{SnF}_4$ , which was previously called stannic fluoride but is now named tin(IV) fluoride.

### *Example 1: Naming Ionic Compounds*

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

1.  $\text{Fe}_2\text{S}_3$
2.  $\text{CuSe}$
3.  $\text{GaN}$
4.  $\text{CrCl}_3$
5.  $\text{Ti}_2(\text{SO}_4)_3$

Show Answer

The anions in these compounds have a fixed negative charge ( $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ,  $\text{N}^{3-}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ ), 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  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ti}^{3+}$ . These charges are used in the names of the metal ions:

1. iron(III) sulfide
2. copper(II) selenide
3. gallium(III) nitride
4. chromium(III) chloride
5. titanium(III) sulfate

## Check Your Learning

Write the formulas of the following ionic compounds:

1. chromium(III) phosphide
2. mercury(II) sulfide
3. manganese(II) phosphate
4. copper(I) oxide
5. chromium(VI) fluoride

Show Answer

1.  $\text{CrP}$
2.  $\text{HgS}$
3.  $\text{Mn}_3(\text{PO}_4)_2$
4.  $\text{Cu}_2\text{O}$
5.  $\text{CrF}_6$

## Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 1) 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.

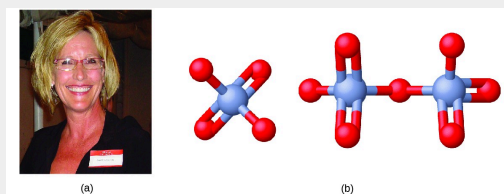


Figure 1. (a) Erin Brokovich found that Cr(IV), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate,  $\text{CrO}_4^{2-}$  (left), and dichromate,  $\text{Cr}_2\text{O}_7^{2-}$  (right).



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.

## Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation

in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

## Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO<sub>2</sub>. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *-ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table 5.

NumberPrefix

---

**Table 5. Nomenclature Prefixes**

Number	Prefix		
1 (sometimes omitted)	mono-	6	hexa-
2	di-	7	hepta-
3	tri-	8	octa-
4	tetra-	9	nona-
5	penta-	10	deca-

---

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO<sub>2</sub> is called carbon dioxide. When two vowels are

adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table 6.

CompoundName

**Table 6. Names of Some Molecular Compounds Composed of Two Elements**

**Compound    Name**

SO <sub>2</sub>	sulfur dioxide	BCl <sub>3</sub>	boron trichloride
SO <sub>3</sub>	sulfur trioxide	SF <sub>6</sub>	sulfur hexafluoride
NO <sub>2</sub>	nitrogen dioxide	PF <sub>5</sub>	phosphorus pentafluoride
N <sub>2</sub> O <sub>4</sub>	dinitrogen tetroxide	P <sub>4</sub> O <sub>10</sub>	tetraphosphorus decaoxide
N <sub>2</sub> O <sub>5</sub>	dinitrogen pentoxide	IF <sub>7</sub>	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N<sub>2</sub>O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H<sub>2</sub>O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

### *Example 2: Naming Covalent Compounds*

Name the following covalent compounds:

1. SF<sub>6</sub>
2. N<sub>2</sub>O<sub>3</sub>
3. Cl<sub>2</sub>O<sub>7</sub>
4. P<sub>4</sub>O<sub>6</sub>

Show Answer

Because these compounds consist solely of nonmetals,

we use prefixes to designate the number of atoms of each element:

1. sulfur hexafluoride
2. dinitrogen trioxide
3. dichlorine heptoxide
4. tetraphosphorus hexoxide

### *Check Your Learning*

Write the formulas for the following compounds:

1. phosphorus pentachloride
2. dinitrogen monoxide
3. iodine heptafluoride
4. carbon tetrachloride

Show Answer

1.  $\text{PCl}_5$
2.  $\text{N}_2\text{O}$
3.  $\text{IF}_7$
4.  $\text{CCl}_4$

The [Chemiste website](#) provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

## 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,  $\text{H}^+$ , when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. 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

For example, when the gas  $\text{HCl}$  (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 7.

---

**Table 7. Names of Some Simple Acids**

Name of Gas	Name of Acid
$\text{HF}(g)$ , hydrogen fluoride	$\text{HF}(aq)$ , hydrofluoric acid
$\text{HCl}(g)$ , hydrogen chloride	$\text{HCl}(aq)$ , hydrochloric acid
$\text{HBr}(g)$ , hydrogen bromide	$\text{HBr}(aq)$ , hydrobromic acid
$\text{HI}(g)$ , hydrogen iodide	$\text{HI}(aq)$ , hydroiodic acid
$\text{H}_2\text{S}(g)$ , hydrogen sulfide	$\text{H}_2\text{S}(aq)$ , 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  $\text{H}_2\text{CO}_3$  (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 8. There are some exceptions to the general naming method (e.g.,  $\text{H}_2\text{SO}_4$  is called sulfuric acid, not sulfic acid, and  $\text{H}_2\text{SO}_3$  is sulfurous, not sulfous, acid).

---

**Table 8. Names of Common Oxyacids**

<b>Formula</b>	<b>Anion Name</b>	<b>Acid Name</b>
$\text{HC}_2\text{H}_3\text{O}_2$	acetate	acetic acid
$\text{HNO}_3$	nitrate	nitric acid
$\text{HNO}_2$	nitrite	nitrous acid
$\text{HClO}_4$	perchlorate	perchloric acid
$\text{H}_2\text{CO}_3$	carbonate	carbonic acid
$\text{H}_2\text{SO}_4$	sulfate	sulfuric acid
$\text{H}_2\text{SO}_3$	sulfite	sulfurous acid
$\text{H}_3\text{PO}_4$	phosphate	phosphoric acid

---

## *Key Concepts and Summary*

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,  $\text{K}_2\text{O}$  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,  $\text{FeCl}_2$  is iron(II) chloride and  $\text{FeCl}_3$  is iron(III) chloride.

Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. 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  $\text{SF}_6$ , sulfur hexafluoride, and  $\text{N}_2\text{O}_4$ , dinitrogen tetroxide. 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;”  $\text{HCl}$  is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *-ic*, and adding “acid;”  $\text{H}_2\text{CO}_3$  is carbonic acid.

## Exercises

1. Name the following compounds:
  - a.  $\text{CsCl}$
  - b.  $\text{BaO}$
  - c.  $\text{K}_2\text{S}$
  - d.  $\text{BeCl}_2$
  - e.  $\text{HBr}$
  - f.  $\text{AlF}_3$
2. Name the following compounds:
  - a.  $\text{NaF}$
  - b.  $\text{Rb}_2\text{O}$
  - c.  $\text{BCl}_3$
  - d.  $\text{H}_2\text{Se}$
  - e.  $\text{P}_4\text{O}_6$
  - f.  $\text{ICl}_3$
3. 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
4. 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
5. 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
6. 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
7. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:
- a.  $\text{Cr}_2\text{O}_3$
  - b.  $\text{FeCl}_2$
  - c.  $\text{CrO}_3$
  - d.  $\text{TiCl}_4$

- e.  $\text{CoO}$
  - f.  $\text{MoS}_2$
8. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:
- a.  $\text{NiCO}_3$
  - b.  $\text{MoO}_3$
  - c.  $\text{Co}(\text{NO}_3)_2$
  - d.  $\text{V}_2\text{O}_5$
  - e.  $\text{MnO}_2$
  - f.  $\text{Fe}_2\text{O}_3$
9. 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)
10. The following ionic compounds are found in common household products. Name each of the compounds:
- a.  $\text{Ca}(\text{H}_2\text{PO}_4)_2$
  - b.  $\text{FeSO}_4$
  - c.  $\text{CaCO}_3$
  - d.  $\text{MgO}$

- e.  $\text{NaNO}_2$
- f.  $\text{KI}$

11. What are the IUPAC names of the following compounds?

- a. manganese dioxide
- b. mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ )
- c. ferric nitrate [ $\text{Fe}(\text{NO}_3)_3$ ]
- d. titanium tetrachloride
- e. cupric bromide ( $\text{CuBr}_2$ )

Show Selected Answers

1. (a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

3. (a)  $\text{RbBr}$ ; (b)  $\text{MgSe}$ ; (c)  $\text{Na}_2\text{O}$ ; (d)  $\text{CaCl}_2$ ; (e)  $\text{HF}$ ; (f)  $\text{GaP}$ ; (g)  $\text{AlBr}_3$ ; (h)  $(\text{NH}_4)_2\text{SO}_4$

5. (a)  $\text{ClO}_2$ ; (b)  $\text{N}_2\text{O}_4$ ; (c)  $\text{K}_3\text{P}$ ; (d)  $\text{Ag}_2\text{S}$ ; (e)  $\text{AlN}$ ; (f)  $\text{SiO}_2$

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

9. (a)  $\text{K}_3\text{PO}_4$ ; (b)  $\text{CuSO}_4$ ; (c)  $\text{CaCl}_2$ ; (d)  $\text{TiO}_2$ ; (e)  $\text{NH}_4\text{NO}_3$ ; (f)  $\text{NaHSO}_4$

11. (a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

## Glossary

**binary acid:** compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release  $\text{H}^+$  ions when dissolved in water)

**binary compound:** compound containing two different elements.

**nomenclature:** system of rules for naming objects of interest

**oxyacid:** compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release  $\text{H}^+$  ions when dissolved in water)

## 29. Hydrocarbons

### *Learning Objectives*

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

- Explain the importance of hydrocarbons and the reason for their diversity
- Name saturated and unsaturated hydrocarbons, and molecules derived from them
- Describe the reactions characteristic of saturated and unsaturated hydrocarbons
- Identify structural and geometric isomers of hydrocarbons

The largest database<sup>1</sup> of organic compounds lists about 10 million substances, which include compounds originating from living organisms and those synthesized by chemists. The number of potential organic compounds has been estimated<sup>2</sup> at  $10^{60}$ —an astronomically high number. The existence of so many organic molecules is a consequence of the ability of carbon atoms to form

1. This is the Beilstein database, now available through the Reaxys site ([www.elsevier.com/online-tools/reaxys](http://www.elsevier.com/online-tools/reaxys)).
2. Peplow, Mark. “Organic Synthesis: The Robo-Chemist,” *Nature* 512 (2014): 20–2.

up to four strong bonds to other carbon atoms, resulting in chains and rings of many different sizes, shapes, and complexities.

The simplest **organic compounds** contain only the elements carbon and hydrogen, and are called hydrocarbons. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

## Alkanes

**Alkanes**, or **saturated hydrocarbons**, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has  $sp^3$  hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane are illustrated in Figure 1. Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line. Because of the  $sp^3$  hybridization, the bond angles in carbon

chains are close to  $109.5^\circ$ , giving such chains in an alkane a zigzag shape.

The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed. Condensed structural formulas for ethane and pentane are shown at the bottom of Figure 1, and several additional examples are provided in the exercises at the end of this chapter.

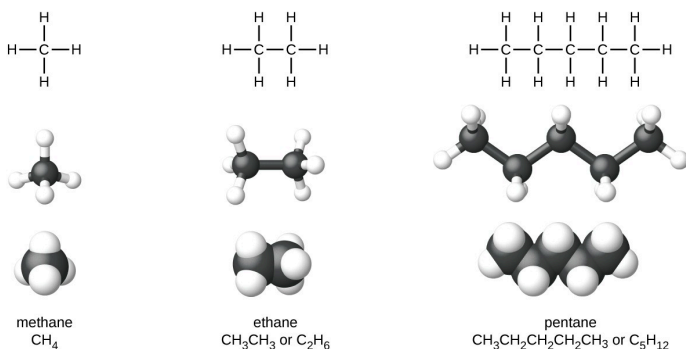


Figure 1. Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

A common method used by organic chemists to simplify the drawings of larger molecules is to use a **skeletal structure** (also called a line-angle structure). In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or bend in a line. Hydrogen atoms are not drawn if they are attached to a carbon. Other atoms besides carbon and hydrogen are represented by their elemental symbols. Figure 2 shows three different ways to draw the same structure.

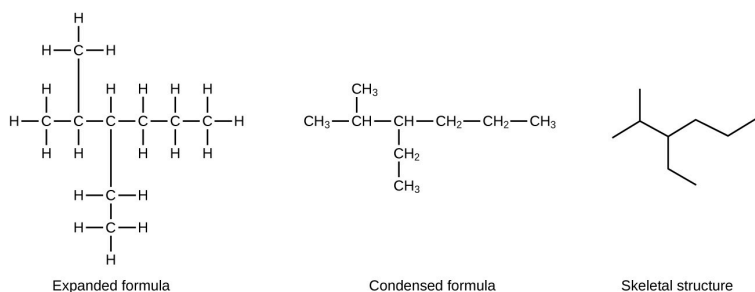
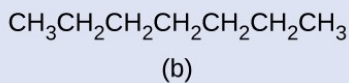
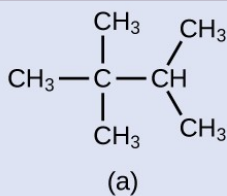


Figure 2. The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

### Example 1: Drawing Skeletal Structures

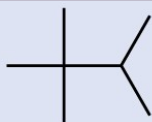
Draw the skeletal structures for these two molecules:



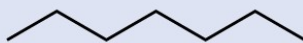
Show Answer

Each carbon atom is converted into the end of a line or the place where lines intersect. All hydrogen atoms attached to the carbon atoms are left out of the structure (although we still need to recognize they are there):





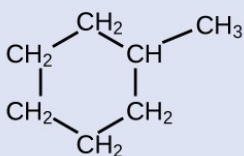
(a)



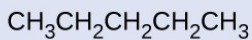
(b)

### Check Your Learning

Draw the skeletal structures for these two molecules:

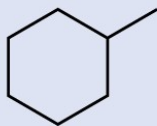


(a)

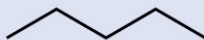


(b)

Show Answer



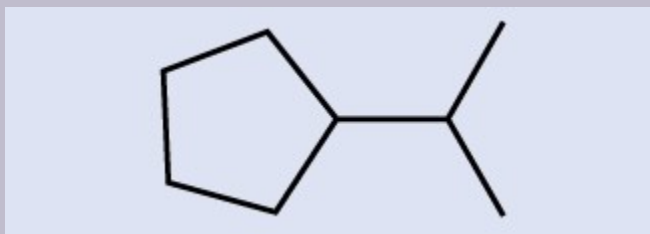
(a)



(b)

### Example 2: Interpreting Skeletal Structures

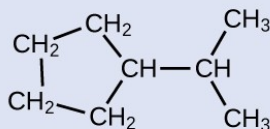
Identify the chemical formula of the molecule represented here:



Show Answer

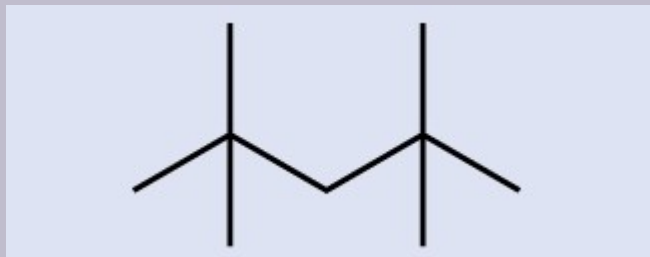
There are eight places where lines intersect or end, meaning that there are eight carbon atoms in the molecule. Since we know that carbon atoms tend to make four bonds, each carbon atom will have the number of hydrogen atoms that are required for four bonds. This compound contains 16 hydrogen atoms for a molecular formula of  $C_8H_{16}$ .

Location of the hydrogen atoms:



### Check Your Learning

Identify the chemical formula of the molecule represented here:



Show Answer

$C_{9}H_{20}$

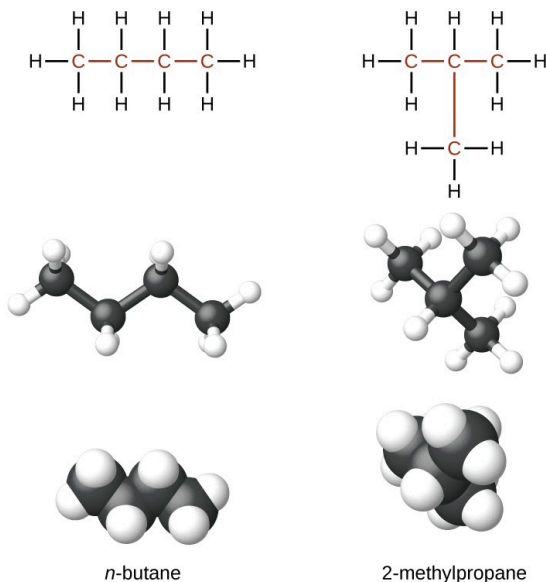
All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of  $C_nH_{2n+2}$ . The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 1) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

**Table 1. Properties of Some Alkanes<sup>3</sup>**

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP <sup>4</sup>	Number of Structural Isomers
methane	CH <sub>4</sub>	-182.5	-161.5	gas	1
ethane	C <sub>2</sub> H <sub>6</sub>	-183.3	-88.6	gas	1
propane	C <sub>3</sub> H <sub>8</sub>	-187.7	-42.1	gas	1
butane	C <sub>4</sub> H <sub>10</sub>	-138.3	-0.5	gas	2
pentane	C <sub>5</sub> H <sub>12</sub>	-129.7	36.1	liquid	3
hexane	C <sub>6</sub> H <sub>14</sub>	-95.3	68.7	liquid	5
heptane	C <sub>7</sub> H <sub>16</sub>	-90.6	98.4	liquid	9
octane	C <sub>8</sub> H <sub>18</sub>	-56.8	125.7	liquid	18
nonane	C <sub>9</sub> H <sub>20</sub>	-53.6	150.8	liquid	35
decane	C <sub>10</sub> H <sub>22</sub>	-29.7	174.0	liquid	75
tetradecane	C <sub>14</sub> H <sub>30</sub>	5.9	253.5	solid	1858
octadecane	C <sub>18</sub> H <sub>38</sub>	28.2	316.1	solid	60,523

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C<sub>4</sub>H<sub>10</sub>: They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:

3. Physical properties for C<sub>4</sub>H<sub>10</sub> and heavier molecules are those of the normal isomer, *n*-butane, *n*-pentane, etc.
4. STP indicates a temperature of 0 °C and a pressure of 1 atm.



The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2-methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 3 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.

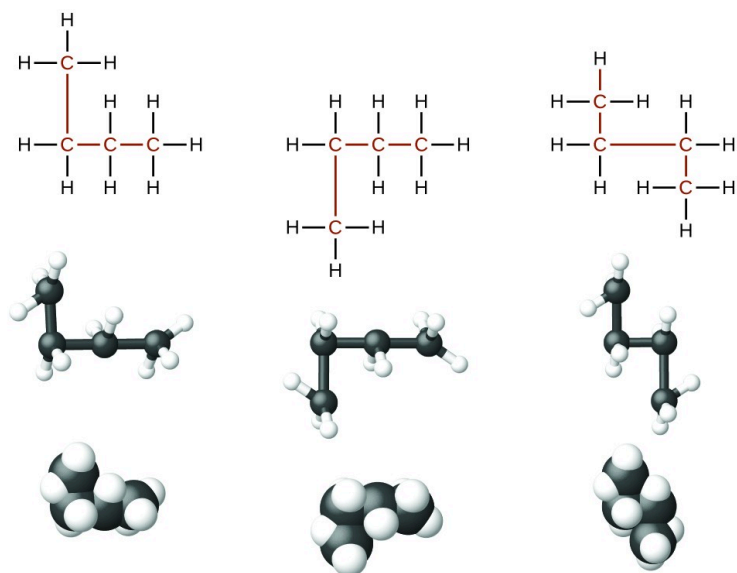


Figure 3. These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

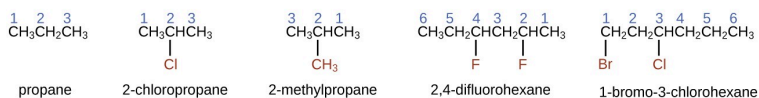
## The Basics of Organic Nomenclature: Naming Alkanes

The International Union of Pure and Applied Chemistry (**IUPAC**) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and

decane (10). These prefixes can be seen in the names of the alkanes described in Table 1.

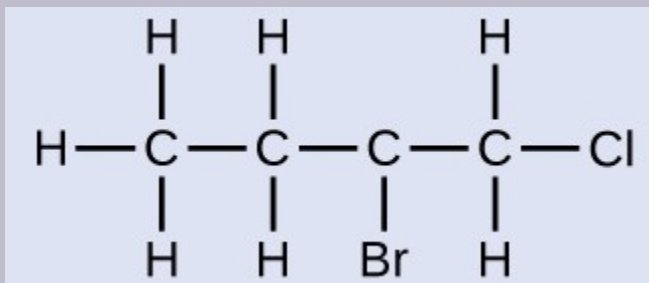
2. Add prefixes to the name of the longest chain to indicate the positions and names of **substituents**. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.



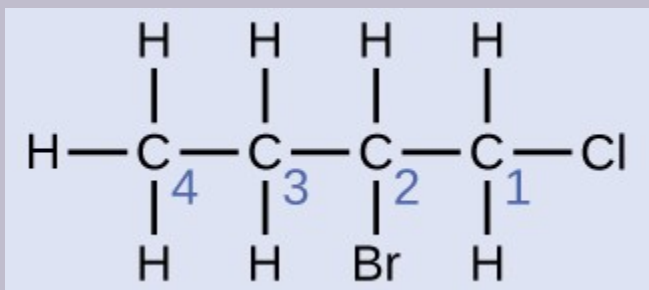
When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), etc. (for example, *difluoro-* indicates two fluoride substituents).

### *Example 3: Naming Halogen-substituted Alkanes*

Name the molecule whose structure is shown here:



Show Answer



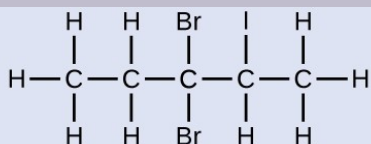
The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms



means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

### *Check Your Learning*

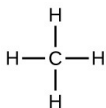
Name the following molecule:



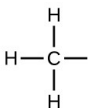
Show Answer

3,3-dibromo-2-iodopentane

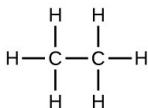
We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an **alkyl group** is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:



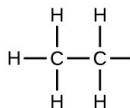
methane



methyl group



ethane

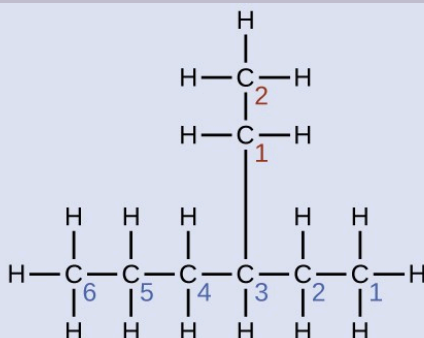


ethyl group

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

### Example 4: Naming Substituted Alkanes

Name the molecule whose structure is shown here:

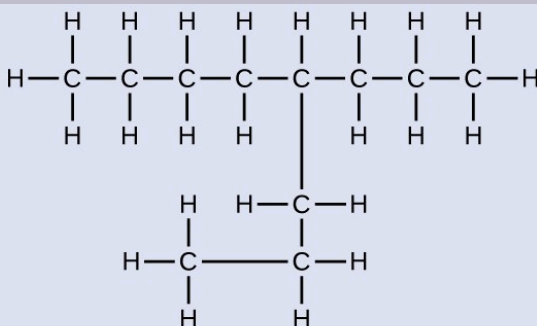


Show Answer

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the red numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in blue)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

## Check Your Learning

Name the following molecule:

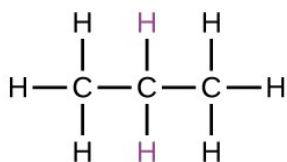


Show Answer

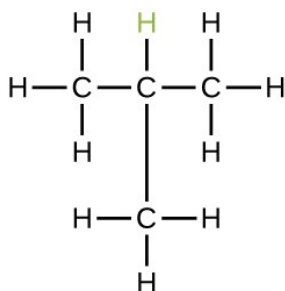
4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in Figure 1. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent (Figure 1) and removing any one of these hydrogen atoms produces an ethyl group. Each of

the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2-methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:



propane



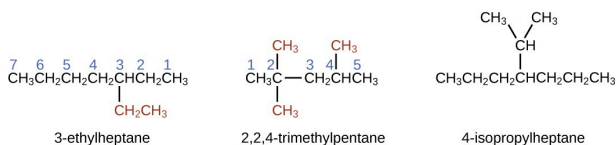
2-methylpropane

Each of the six equivalent hydrogen atoms of the first type in propane and each of the nine equivalent hydrogen atoms of that type in 2-methylpropane (all shown in black) are bonded to a carbon atom that is bonded to only one other carbon atom. The two purple hydrogen atoms in propane are of a second type. They differ from the six hydrogen atoms of the first type in that they are bonded to a carbon atom bonded to two other carbon atoms. The green hydrogen atom in 2-methylpropane differs from the other nine hydrogen atoms in that molecule and from the purple hydrogen atoms in propane. The green hydrogen atom in 2-methylpropane is bonded to a carbon atom bonded to three other carbon atoms. Two different alkyl groups can be formed from each of these molecules, depending on which hydrogen atom is removed. The names and structures of these and several other alkyl groups are listed in Figure 4.

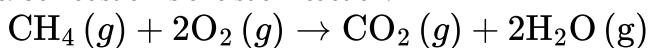
Alkyl Group	Structure
methyl	$\text{CH}_3\text{—}$
ethyl	$\text{CH}_3\text{CH}_2\text{—}$
<i>n</i> -propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$
isopropyl	$\begin{array}{c}   \\ \text{CH}_3\text{CHCH}_3 \end{array}$
<i>n</i> -butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
sec-butyl	$\begin{array}{c}   \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$
isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{—} \\   \\ \text{CH}_3 \end{array}$
<i>tert</i> -butyl	$\begin{array}{c}   \\ \text{CH}_3\text{CCH}_3 \\   \\ \text{CH}_3 \end{array}$

Figure 4. This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C-H or C-C single bonds. Combustion is one such reaction:



Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane,  $\text{CH}_4$ , is the principal component of natural gas. Butane,  $\text{C}_4\text{H}_{10}$ , used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (see Figure 5). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

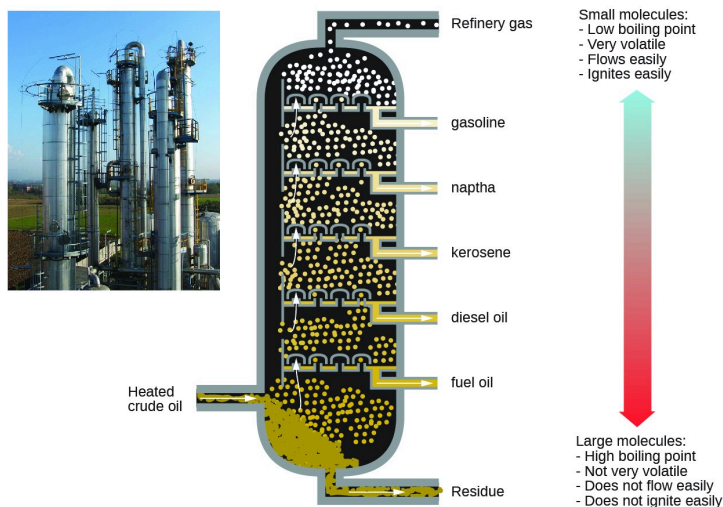
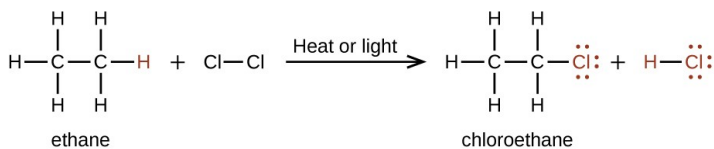


Figure 5. In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a **substitution reaction**, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:



The C-Cl portion of the chloroethane molecule is an example of

a **functional group**, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

Want more practice naming alkanes? Watch this brief video tutorial to review the nomenclature process.



One or more interactive elements has been excluded from this version of the text. You

can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=50#oembed-1>

## Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called **alkenes**. Carbon atoms linked by a double bond are bound together by two bonds, one  $\sigma$  bond and one  $\pi$  bond. Double and triple bonds give rise to a different geometry around the carbon atom that



participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene,  $C_2H_4$ , is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 6); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

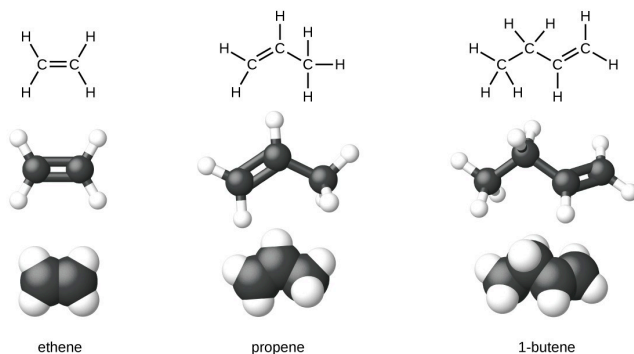


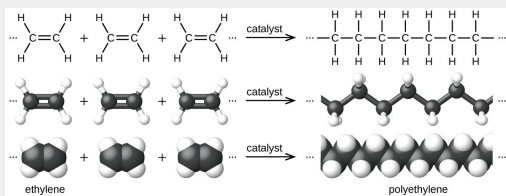
Figure 6. Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

## Everyday Life: Recycling Plastics

Polymers (from Greek words *poly* meaning “many” and *mer* meaning “parts”) are large molecules made up of repeating units, referred to as monomers. Polymers can be natural (starch is a polymer of sugar residues and proteins are polymers of amino acids) or synthetic [like polyethylene, polyvinyl chloride (PVC), and polystyrene]. The variety of structures of polymers translates into a broad range of properties and uses that make them integral parts of our everyday lives. Adding functional groups to the structure of a polymer can result in significantly different properties (see Chemistry in Everyday Life: Kevlar, later in this chapter).

An example of a polymerization reaction is shown in Figure 7. The monomer ethylene ( $\text{C}_2\text{H}_4$ ) is a gas at room temperature, but when polymerized, using a transition metal catalyst, it is transformed into a solid material made up of long chains of  $-\text{CH}_2-$  units called polyethylene. Polyethylene is a commodity plastic used primarily for packaging (bags and films).



*Figure 7. The reaction for the polymerization of ethylene to polyethylene is shown.*

Polyethylene is a member of one subset of synthetic polymers classified as plastics. Plastics are synthetic organic solids that can be molded; they are typically organic polymers with high molecular masses. Most of the monomers that go into common plastics (ethylene, propylene, vinyl chloride, styrene, and ethylene terephthalate) are derived from petrochemicals and are not very biodegradable, making them candidate materials for recycling. Recycling plastics helps minimize the need for using more of the petrochemical supplies and also minimizes the environmental damage caused by throwing away these nonbiodegradable materials.

Plastic recycling is the process of recovering waste, scrap, or used plastics, and reprocessing the material into useful products. For example, polyethylene terephthalate (soft drink bottles) can be melted down and used for plastic furniture, in carpets, or for other applications. Other plastics, like polyethylene (bags) and polypropylene (cups, plastic food containers), can be

recycled or reprocessed to be used again. Many areas of the country have recycling programs that focus on one or more of the commodity plastics that have been assigned a recycling code (see Figure 8). These operations have been in effect since the 1970s and have made the production of some plastics among the most efficient industrial operations today.








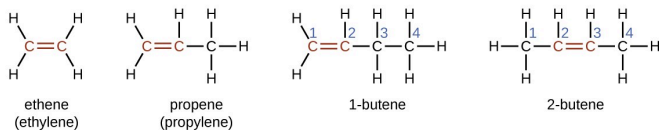
 1 PETE	polyethylene terephthalate (PETE)	Soda bottles and oven-ready food trays
 2 HDPE	high-density polyethylene (HDPE)	Bottles for milk and dishwashing liquids
 3 V	polyvinyl chloride (PVC)	Food trays, plastic wrap, bottles for mineral water and shampoo
 4 LDPE	low density polyethylene (LDPE)	Shopping bags and garbage bags
 5 PP	polypropylene (PP)	Margarine tubs, microwaveable food trays
 6 PS	polystyrene (PS)	Yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, packaging for electronics and toys
 7 OTHER	any other plastics (OTHER)	Plastics that do not fall into any of the above categories One example is melamine resin (plastic plates, plastic cups)

Figure 8. Each type of recyclable plastic is imprinted with a code for easy identification.

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



## Isomers of Alkenes

Molecules of 1-butene and 2-butene are structural isomers; the arrangement of the atoms in these two molecules differs. As an example of arrangement differences, the first carbon atom in 1-butene is bonded to two hydrogen atoms; the first carbon atom in 2-butene is bonded to three hydrogen atoms.

The compound 2-butene and some other alkenes also form a second type of isomer called a geometric isomer. In a set of geometric isomers, the same types of atoms are attached to each other in the same order, but the geometries of the two molecules differ. Geometric isomers of alkenes differ in the orientation of the groups on either side of a  $\text{C} = \text{C}$  bond.

Carbon atoms are free to rotate around a single bond but not around a double bond; a double bond is rigid. This makes it possible to have two isomers of 2-butene, one with both methyl groups on the same side of the double bond and one with the methyl groups on opposite sides. When structures of butene are drawn with  $120^\circ$  bond angles around the  $\text{sp}^2$ -hybridized carbon atoms participating in the double bond, the isomers are apparent. The 2-butene isomer in which the two methyl groups are on the same side is called a *cis*-isomer; the one in which the two methyl groups are on opposite sides is called a *trans*-isomer (Figure 9). The different geometries produce different physical properties, such as boiling point, that may make separation of the isomers possible:

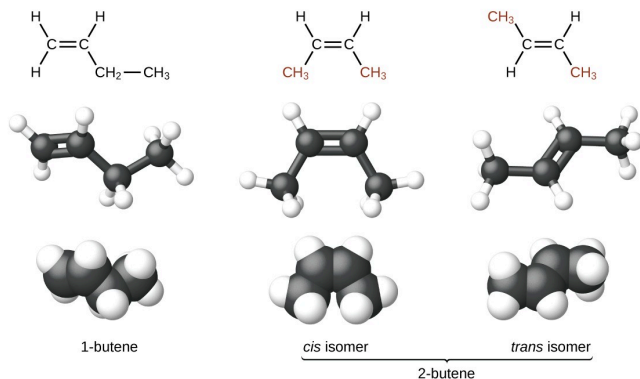
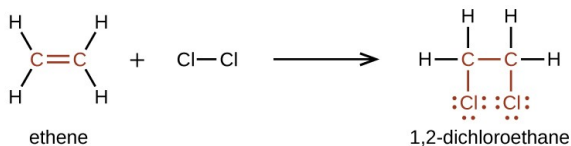


Figure 9. These molecular models show the structural and geometric isomers of butene.

Alkenes are much more reactive than alkanes because the  $\text{C}=\text{C}$  moiety is a reactive functional group. A  $\pi$  bond, being a weaker bond, is disrupted much more easily than a  $\sigma$  bond. Thus, alkenes undergo a characteristic reaction in which the  $\pi$  bond is broken and replaced by two  $\sigma$  bonds. This reaction is called an addition reaction. The hybridization of the carbon atoms in the double bond in an alkene changes from  $sp^2$  to  $sp^3$  during an addition reaction. For example, halogens add to the double bond in an alkene instead of replacing hydrogen, as occurs in an alkane:



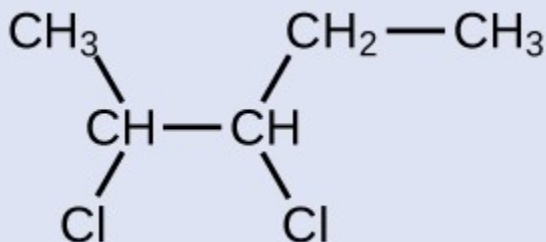
### Example 5: Alkene Reactivity and Naming

Provide the IUPAC names for the reactant and product of the halogenation reaction shown here:



Show Answer

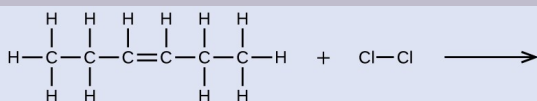
The reactant is a five-carbon chain that contains a carbon-carbon double bond, so the base name will be pentene. We begin counting at the end of the chain closest to the double bond—in this case, from the left—the double bond spans carbons 2 and 3, so the name becomes 2-pentene. Since there are two carbon-containing groups attached to the two carbon atoms in the double bond—and they are on the same side of the double bond—this molecule is the *cis*-isomer, making the name of the starting alkene *cis*-2-pentene. The product of the halogenation reaction will have two chlorine atoms attached to the carbon atoms that were a part of the carbon-carbon double bond:



This molecule is now a substituted alkane and will be named as such. The base of the name will be pentane. We will count from the end that numbers the carbon atoms where the chlorine atoms are attached as 2 and 3, making the name of the product 2,3-dichloropentane.

### *Check Your Learning*

Provide names for the reactant and product of the reaction shown:



Show Answer

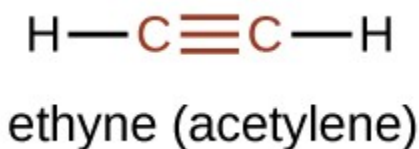
reactant: trans-3-hexene, product: 3,4-dichlorohexane



## Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one  $\sigma$  bond and two  $\pi$  bonds. The  $sp$ -hybridized carbons involved in the triple bond have bond angles of  $180^\circ$ , giving these types of bonds a linear, rod-like shape.

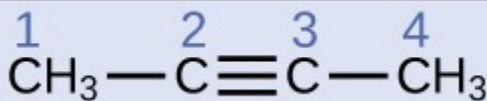
The simplest member of the alkyne series is ethyne,  $C_2H_2$ , commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:



The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example,  $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$  is called 1-butyne.

### *Example 6: Structure of Alkynes*

Describe the geometry and hybridization of the carbon atoms in the following molecule:

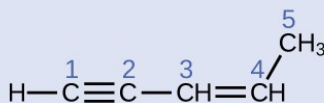


Show Answer

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with  $sp^3$  hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as  $sp$  hybrids.

### Check Your Learning

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:

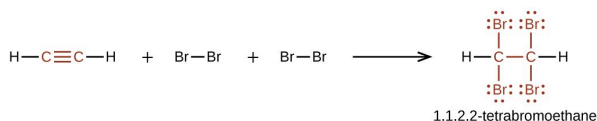


Show Answer

carbon 1:  $sp$ ,  $180^\circ$ ; carbon 2:  $sp$ ,  $180^\circ$ ; carbon 3:  $sp^2$ ,  $120^\circ$ ;  
carbon 4:  $sp^2$ ,  $120^\circ$ ; carbon 5:  $sp^3$ ,  $109.5^\circ$

Chemically, the alkynes are similar to the alkenes. Since the  $\text{C} \equiv \text{C}$  functional group has two  $\pi$  bonds, alkynes typically react even more readily, and react with twice as much reagent in addition

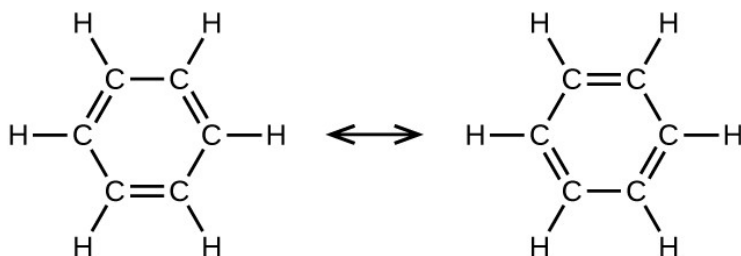
reactions. The reaction of acetylene with bromine is a typical example:



Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

## Aromatic Hydrocarbons

Benzene,  $\text{C}_6\text{H}_6$ , is the simplest member of a large family of hydrocarbons, called **aromatic hydrocarbons**. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene,  $\text{C}_6\text{H}_6$ , are:



Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of

$sp^2$ -hybridized carbon atoms with the unhybridized  $p$  orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the  $sp^2$  hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of  $\sigma$  bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized  $p$  orbitals to yield the  $\pi$  bonds.

Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C-C single bond and a C=C double bond. To

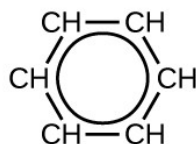
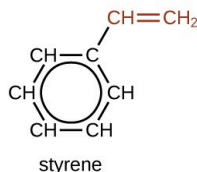
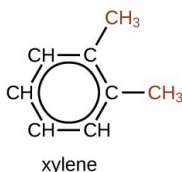
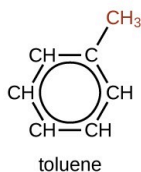


Figure 10. This condensed formula shows the unique bonding structure of benzene.

represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure 10.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:

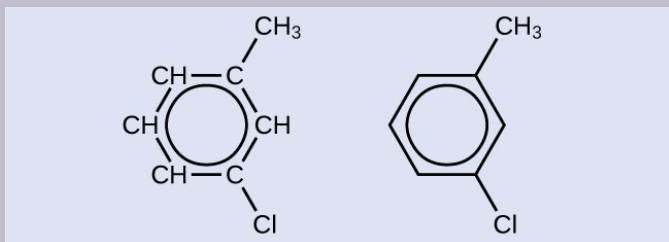


Toluene and xylene are important solvents and raw materials in

the chemical industry. Styrene is used to produce the polymer polystyrene.

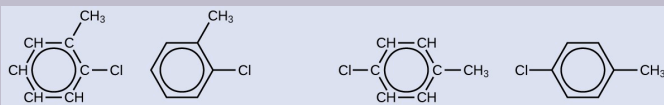
### *Example 7: Structure of Aromatic Hydrocarbons*

One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



Show Answer

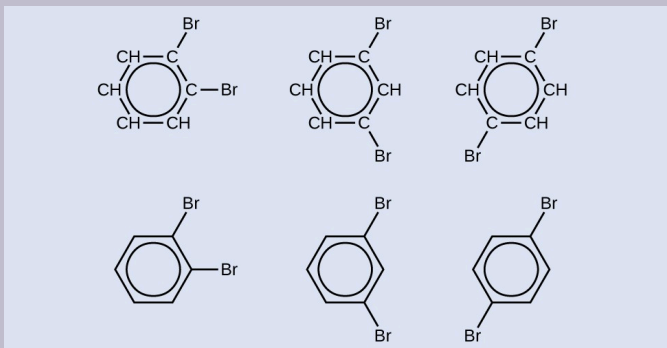
Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:



### Check Your Learning

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Show Answer



### Key Concepts and Summary

Strong, stable bonds between carbon atoms produce complex molecules containing chains, branches, and rings.

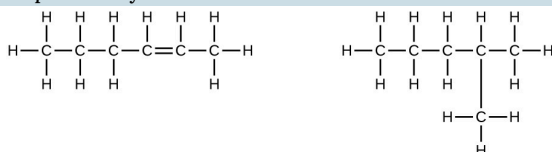
The chemistry of these compounds is called organic chemistry. Hydrocarbons are organic compounds composed of only carbon and hydrogen. The alkanes are saturated hydrocarbons—that is, hydrocarbons that contain only single bonds. Alkenes contain one or more carbon-carbon double bonds. Alkynes contain one or more carbon-carbon triple bonds. Aromatic hydrocarbons contain ring structures with delocalized  $\pi$  electron systems.

## *Exercises*

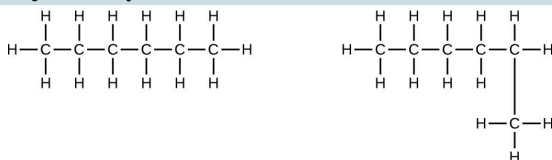
1. Write the chemical formula and Lewis structure of the following, each of which contains five carbon atoms:
  - a. an alkane
  - b. an alkene
  - c. an alkyne
2. What is the difference between the hybridization of carbon atoms' valence orbitals in saturated and unsaturated hydrocarbons?
3. On a microscopic level, how does the reaction of bromine with a saturated hydrocarbon differ from its reaction with an unsaturated hydrocarbon? How are they similar?
4. On a microscopic level, how does the reaction of bromine with an alkene differ from its reaction with an alkyne? How are they similar?

5. Explain why unbranched alkenes can form geometric isomers while unbranched alkanes cannot. Does this explanation involve the macroscopic domain or the microscopic domain?

6. Explain why these two molecules are not isomers:



7. Explain why these two molecules are not isomers:

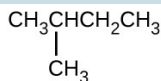


8. How does the carbon-atom hybridization change when polyethylene is prepared from ethylene?
9. Write the Lewis structure and molecular formula for each of the following hydrocarbons:
- hexane
  - 3-methylpentane
  - cis-3-hexene
  - 4-methyl-1-pentene
  - 3-hexyne
  - 4-methyl-2-pentyne
10. Write the chemical formula, condensed formula, and Lewis structure for each of the following hydrocarbons:
- heptane
  - 3-methylhexane

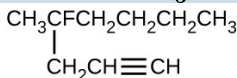


- c. *trans*-3-heptene
- d. 4-methyl-1-hexene
- e. 2-heptyne
- f. 3,4-dimethyl-1-pentyne

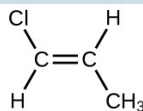
11. Give the complete IUPAC name for each of the following compounds:



c.



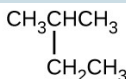
e.



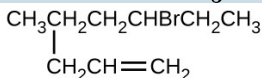
f.



12. Give the complete IUPAC name for each of the following compounds:



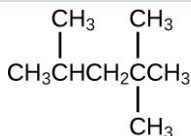
c.



e.



13. Butane is used as a fuel in disposable lighters. Write the Lewis structure for each isomer of butane.
14. Write Lewis structures and name the five structural isomers of hexane.
15. Write Lewis structures for the *cis-trans* isomers of  $\text{CH}_3\text{CH}=\text{CHCl}$ .
16. Write structures for the three isomers of the aromatic hydrocarbon xylene,  $\text{C}_6\text{H}_4(\text{CH}_3)_2$ .
17. Isooctane is the common name of the isomer of  $\text{C}_8\text{H}_{18}$  used as the standard of 100 for the gasoline octane rating:



- a. What is the IUPAC name for the compound?
  - b. Name the other isomers that contain a five-carbon chain with three methyl substituents.
18. Write Lewis structures and IUPAC names for the alkyne isomers of  $\text{C}_4\text{H}_6$ .
19. Write Lewis structures and IUPAC names for all isomers of  $\text{C}_4\text{H}_9\text{Cl}$ .
20. Name and write the structures of all isomers of the propyl and butyl alkyl groups.
21. Write the structures for all the isomers of the  $-\text{C}_5\text{H}_{11}$  alkyl group.
22. Write Lewis structures and describe the molecular geometry at each carbon atom in the following compounds:
  - a. *cis*-3-hexene

- b. *cis*-1-chloro-2-bromoethene
  - c. 2-pentyne
  - d. *trans*-6-ethyl-7-methyl-2-octene
23. Benzene is one of the compounds used as an octane enhancer in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene:  $3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$ . Draw Lewis structures for these compounds, with resonance structures as appropriate, and determine the hybridization of the carbon atoms in each.
24. Teflon is prepared by the polymerization of tetrafluoroethylene. Write the equation that describes the polymerization using Lewis symbols.
25. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.
- a. 1 mol of 1-butyne reacts with 2 mol of iodine.
  - b. Pentane is burned in air.
26. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.
- a. 2-butene reacts with chlorine.
  - b. benzene burns in air.
27. What mass of 2-bromopropane could be prepared from 25.5 g of propene? Assume a 100% yield of product.
28. Acetylene is a very weak acid; however, it will react with moist silver(I) oxide and form water and a compound composed of silver and carbon. Addition

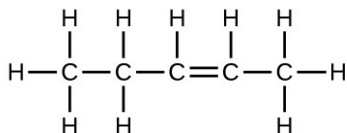
of a solution of HCl to a 0.2352-g sample of the compound of silver and carbon produced acetylene and 0.2822 g of AgCl.

- a. What is the empirical formula of the compound of silver and carbon?
  - b. The production of acetylene on addition of HCl to the compound of silver and carbon suggests that the carbon is present as the acetylide ion,  $\text{C}_2^{2-}$ . Write the formula of the compound showing the acetylide ion.
29. Ethylene can be produced by the pyrolysis of ethane:  $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ . How many kilograms of ethylene is produced by the pyrolysis of  $1.000 \times 10^3 \text{ kg}$  of ethane, assuming a 100.0% yield?

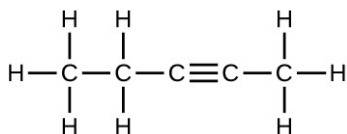
Show Selected Answers

1. There are several sets of answers; one is:

- a.  $\text{C}_5\text{H}_1$
- b.  $\text{C}_5\text{H}_{10}$



- c.  $\text{C}_5\text{H}_8$



3. Both reactions result in bromine being incorporated

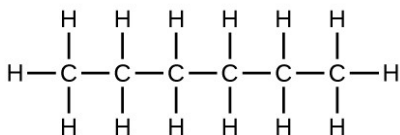
into the structure of the product. The difference is the way in which that incorporation takes place. In the saturated hydrocarbon, an existing C–H bond is broken, and a bond between the C and the Br can then be formed. In the unsaturated hydrocarbon, the only bond broken in the hydrocarbon is the  $\pi$  bond whose electrons can be used to form a bond to one of the bromine atoms in Br<sub>2</sub> (the electrons from the Br–Br bond form the other C–Br bond on the other carbon that was part of the  $\pi$  bond in the starting unsaturated hydrocarbon).

5. Unbranched alkanes have free rotation about the C–C bonds, yielding all orientations of the substituents about these bonds equivalent, interchangeable by rotation. In the unbranched alkenes, the inability to rotate about the C=C bond results in fixed (unchanging) substituent orientations, thus permitting different isomers. Since these concepts pertain to phenomena at the molecular level, this explanation involves the microscopic domain.

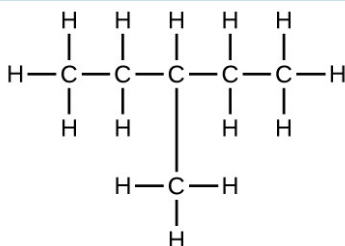
7. They are the same compound because each is a saturated hydrocarbon containing an unbranched chain of six carbon atoms.

9. The Lewis structures and molecular formulas are as follows:

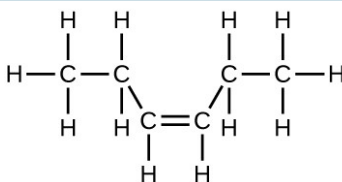
a. C<sub>6</sub>H<sub>14</sub>



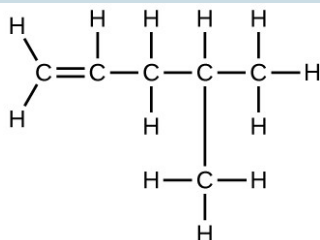
b. C<sub>6</sub>H<sub>14</sub>



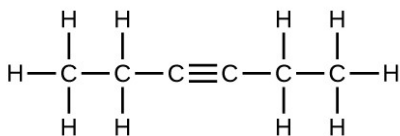
c.  $C_6H_{12}$



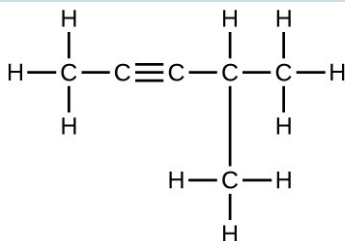
d.  $C_6H_{12}$



e.  $C_6H_{10}$



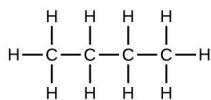
f.  $C_6H_{10}$



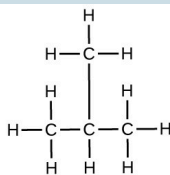
11. The IUPAC names are as follows:

- 2,2-dibromobutane
- 2-chloro-2-methylpropane
- 2-methylbutane
- 1-butyne
- 4-fluoro-4-methyl-1-octyne
- trans*-1-chloropropene
- 5-methyl-1-pentene

13.

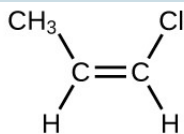


*n*-butane

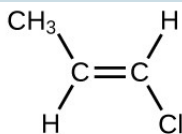


2-methylpropane

15.



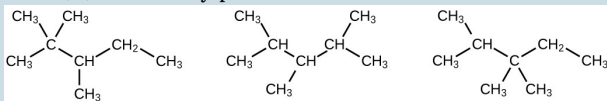
*cis*-



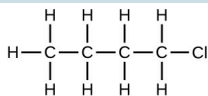
*trans*-

17. The answers are as follows:

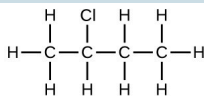
- a. 2,2,4-trimethylpentane  
 b. 2,2,3-trimethylpentane, 2,3,4-trimethylpentane,  
 and 2,3,3-trimethylpentane:



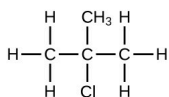
19.



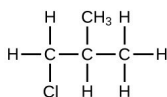
1-chlorobutane



2-chlorobutane

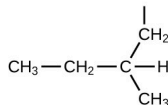
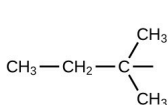
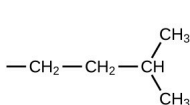
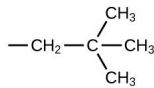
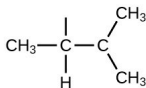
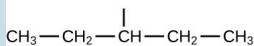
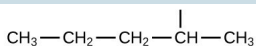
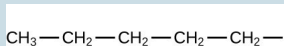


2-chloro-2-methylpropane



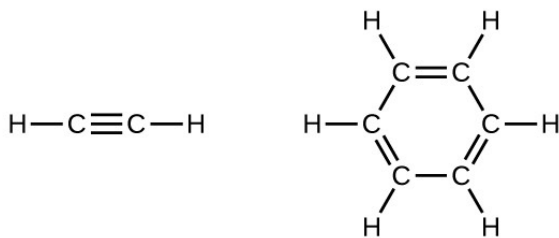
1-chloro-2-methylpropane  
 (1-chloro-2-methylpropane)

21. In the following, the carbon backbone and the appropriate number of hydrogen atoms are shown in condensed form:



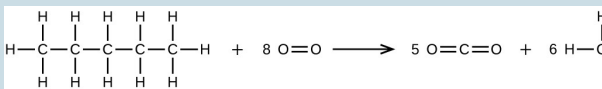
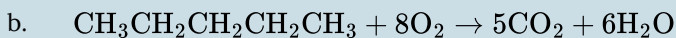
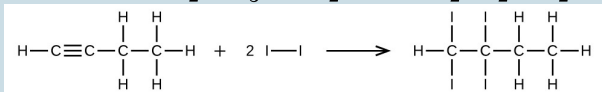
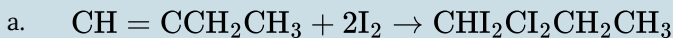
23.





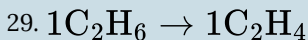
In acetylene, the bonding uses  $sp$  hybrids on carbon atoms and  $s$  orbitals on hydrogen atoms. In benzene, the carbon atoms are  $sp^2$  hybridized.

25. The balanced equations are as follows:



27.

$$\text{C}_3\text{H}_7\text{Br mass} = 22.5\text{g} \times \frac{1\text{molC}_3\text{H}_6}{48.081\text{gC}_3\text{H}_6} \times \frac{1\text{molC}_3\text{H}_7\text{Br}}{1\text{molC}_3\text{H}_6} \times \frac{122.993\text{gC}_3\text{H}_7\text{Br}}{1\text{molC}_3\text{H}_7\text{Br}} = 65.2\text{g}$$



$$\begin{aligned} \text{mass of ethylene} &= 1 \times 10^3\text{kg} \times \frac{1\text{mol}}{30.07\text{g}} \times \frac{28.05\text{g}}{1\text{mol}} \\ &= 9.328 \times 10^2\text{kg} \end{aligned}$$

## Glossary

**alkane:** molecule consisting of only carbon and hydrogen atoms connected by single ( $\sigma$ ) bonds

**alkene:** molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

**alkyl group:** substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

**alkyne:** molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

**aromatic hydrocarbon:** cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

**functional group:** part of an organic molecule that imparts a specific chemical reactivity to the molecule

**organic compound:** natural or synthetic compound that contains carbon

**saturated hydrocarbon:** molecule containing carbon and hydrogen that has only single bonds between carbon atoms

**skeletal structure:** shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

**substituent:** branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

**substitution reaction:** reaction in which one atom replaces another in a molecule

PART VII

# CHEMICAL BONDING AND MOLECULAR SHAPES



## 30. 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,  $\text{Cl}_2$ , 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 1). 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.

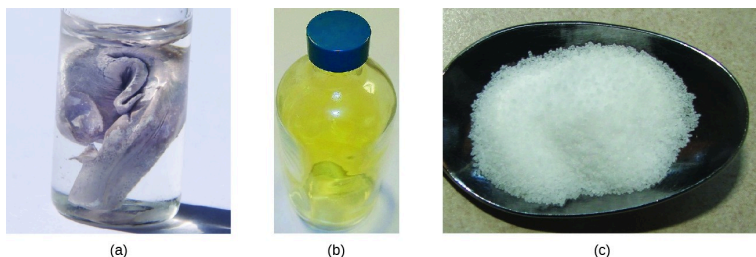


Figure 1. (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by “Jurii”/Wikimedia Commons)

## 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,  $\text{NaCl}$  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,  $\text{Al}_2\text{O}_3$ , indicates that this ionic compound contains two aluminum cations,  $\text{Al}^{3+}$ , for every three oxide anions,  $\text{O}^{2-}$  [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 ( $\text{NaCl}$ ) “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  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions (Figure 2).

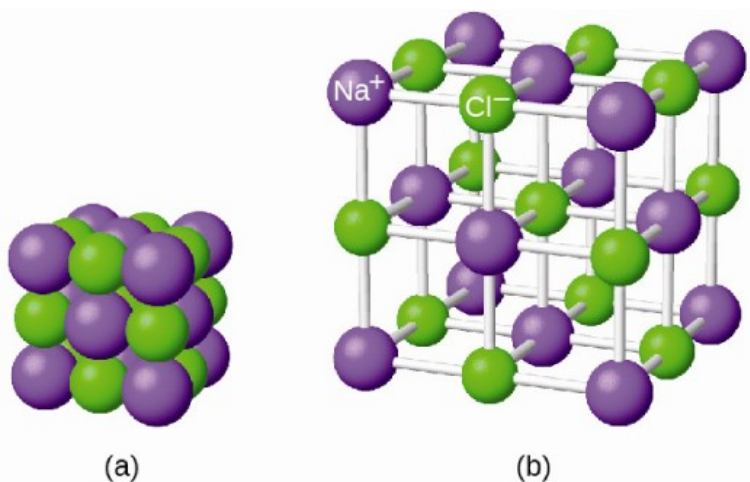
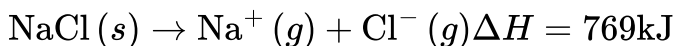


Figure 2. The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is “bonded” to all of the surrounding ions—six in this case.

The strong electrostatic attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions:



## Electronic Structures of Cations

When forming a cation, an atom of a 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  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ . 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  $1s^2 2s^2 2p^6 3s^2 3p^6$ . The  $\text{Ca}^{2+}$  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 ( $\text{Al}^{3+}$ ).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions  $\text{Tl}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{4+}$ , and  $\text{Bi}^{5+}$ , a partial loss of these atoms' valence shell electrons can also lead to the formation of  $\text{Tl}^{+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$  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 behavior: it forms a diatomic ion,  $\text{Hg}_2^{2+}$  (an ion formed from two mercury atoms, with an Hg–Hg bond), in addition to the expected monatomic ion  $\text{Hg}^{2+}$  (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  $\text{Fe}^{2+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ ) by the loss of the  $4s$  electron and the ion  $\text{Fe}^{3+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ) by the loss of the  $4s$  electron and one of the  $3d$  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

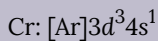
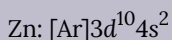
when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost s electrons and a d or f electron.

### *Example 1: Determining the Electronic Structures of Cations*

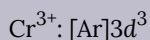
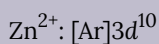
There are at least 14 elements categorized as “essential trace elements” for the human body. They are called “essential” because they are required for healthy bodily functions, “trace” because they are required only in small amounts, and “elements” in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$ . Write the electron configurations of these cations.

Show Answer

First, write the electron configuration for the neutral atoms:



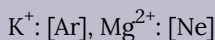
Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the s orbital first and then from the d orbital. For the p-block elements, electrons are removed from the p orbitals and then from the s orbital. Zinc is a member of group 12, so it should have 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:



### *Check Your Learning*

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Show Answer



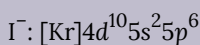
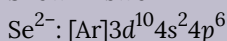
## Electronic Structures of Anions

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  $1s^2 2s^2 2p^4$ , whereas the oxygen anion has the electron configuration of the noble gas neon (Ne),  $1s^2 2s^2 2p^6$ . The two additional electrons required to fill the valence orbitals give the oxide ion the charge of  $2-$  ( $\text{O}^{2-}$ ).

## *Example 2: Determining the Electronic Structure of Anions*

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

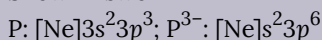
Show Answer



### *Check Your Learning*

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Show Answer



## *Key Concepts and Summary*

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.

## *Exercises*

1. Does a cation gain protons to form a positive charge or does it lose electrons?
2. Iron(III) sulfate  $[\text{Fe}_2(\text{SO}_4)_3]$  is composed of  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  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?
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

6. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
- I
  - Sr
  - K
  - N
  - S
  - In
7. Write the electron configuration for each of the following ions:
- $\text{As}^{3-}$
  - $\text{I}^-$
  - $\text{Be}^{2+}$
  - $\text{Cd}^{2+}$
  - $\text{O}^{2-}$
  - $\text{Ga}^{3+}$
  - $\text{Li}^+$
  - $\text{N}^{3-}$
  - $\text{Sn}^{2+}$
  - $\text{Co}^{2+}$
  - $\text{Fe}^{2+}$
  - $\text{As}^{3+}$
8. Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):
- Cl
  - Na
  - 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

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.)

#### Selected Answers

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.

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.

5. The predicted charges are as follows:

- a.  $P^{3-}$

- b.  $\text{Mg}^{2+}$
- c.  $\text{Al}^{3+}$
- d.  $\text{O}^{2-}$
- e.  $\text{Cl}^-$
- f.  $\text{Cs}^+$

7. The correct electron configurations are

- a.  $[\text{Ar}] 3d^{10}4p^6$
- b.  $[\text{Kr}] 4d^{10}5s^25p^6$
- c.  $1s^2$
- d.  $[\text{Kr}] 4d^8$
- e.  $[\text{He}] 2s^22p^6$
- f.  $[\text{Ar}] 3d^{10}$
- g.  $1s^2$
- h.  $[\text{He}] 2s^22p^6$
- i.  $[\text{Kr}] d^{10}5s^2$
- j.  $[\text{Ar}] 3d^7$
- k.  $[\text{Ar}] 3d^6$
- l.  $[\text{Ar}] 3d^{10}4s^2$

9. The correct electron configurations are

- a.  $1s^22s^22p^63s^23p^1$ ;  $\text{Al}^{3+} 1s^22s^22p^6$
- b.  $1s^22s^22p^63s^23p^63d^{10}4s^24p^5$ ;  
 $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$
- c.  $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$ ;  $\text{Sr}^{2+}$   
 $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$
- d.  $1s^22s^1$ ;  $\text{Li}^+ 1s^2$
- e.  $1s^22s^22p^63s^23p^63d^{10}4s^24p^3$ ;  
 $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$
- f.  $1s^22s^22p^63s^23p^4$ ;  $1s^22s^22p^63s^23p^6$



## Glossary

**inert pair effect:** tendency of heavy atoms to form ions in which their valence s electrons are not lost

**ionic bond:** strong electrostatic force of attraction between cations and anions in an ionic compound

# 31. 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  $\text{H}_2$  molecule; each hydrogen atom in the  $\text{H}_2$  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.

## 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 1 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 ( $1s$ ) 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.

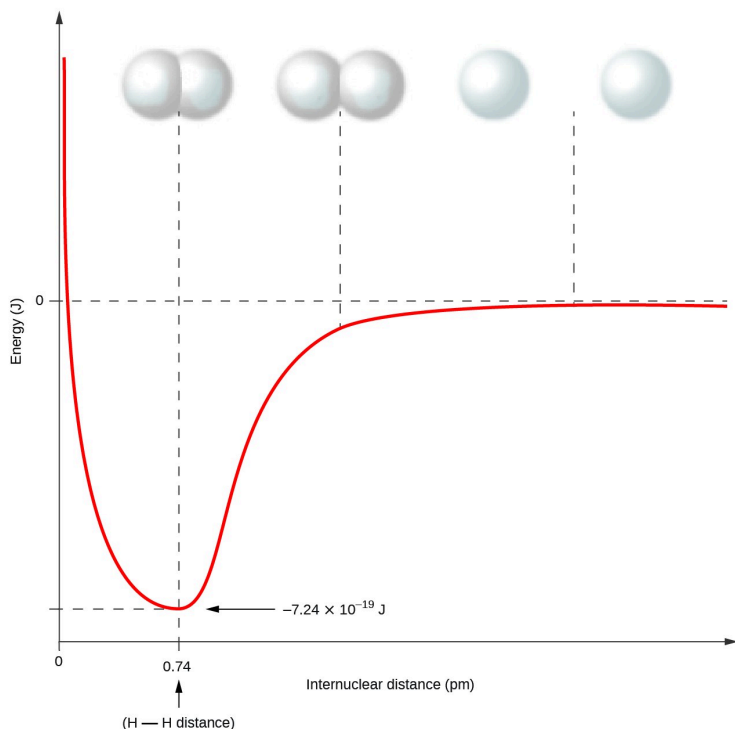
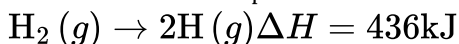
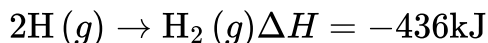


Figure 1. The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

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  $\text{H}_2$ , 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:



Conversely, the same amount of energy is released when one mole of  $\text{H}_2$  molecules forms from two moles of H atoms:



## Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in  $\text{H}_2$ ,  $\text{Cl}_2$ , and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **pure covalent bond**. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of  $\text{Cl}_2$ , each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:



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,  $\text{Cl}_2$  also features a pure 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

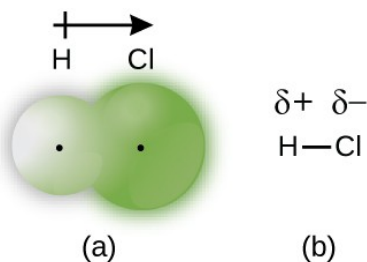


Figure 2. (a) The distribution of electron density in the  $\text{HCl}$  molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols  $\delta^+$  and  $\delta^-$  indicate the polarity of the  $\text{H}-\text{Cl}$  bond.

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 2 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 1, which shows the even distribution of electrons in the H<sub>2</sub> nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,”  $\Delta$ , with a plus sign or minus sign to indicate whether the atom has a partial positive charge ( $\Delta^+$ ) or a partial negative charge ( $\Delta^-$ ). This symbolism is shown for the H–Cl molecule in Figure 2.

## 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) towards 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 3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 4). 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<sub>2</sub> do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

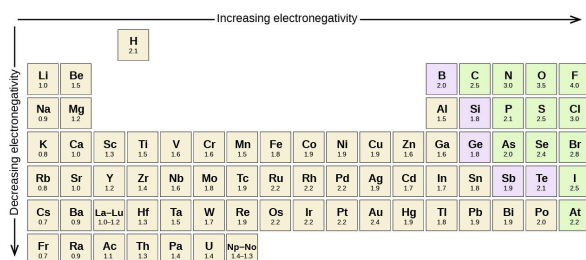


Figure 3. The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

## 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.

## Portrait of a Chemist: Linus Pauling

Linus Pauling, shown in Figure 4, 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.





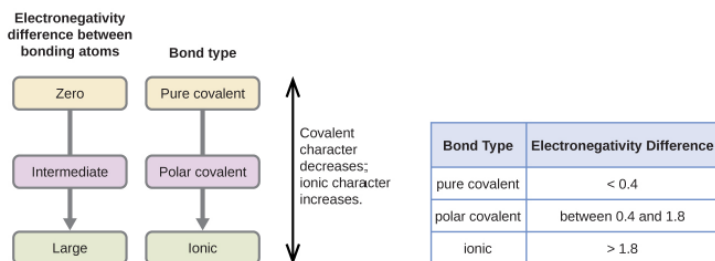
*Figure 4. Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.*

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 ( $\Delta EN$ ) 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 5 shows the relationship between electronegativity difference and bond type.



**Figure 7.8** As the electronegativity difference increases between two atoms, the bond becomes more ionic.

*Figure 5. As the electronegativity difference increases between two atoms, the bond becomes more ionic.*

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 5. 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  $\text{NH}_3$  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  $\text{MnI}_2$  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  $\text{OH}^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , 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,  $\text{KNO}_3$ , contains the  $\text{K}^+$  cation and the polyatomic  $\text{NO}_3^-$  anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions  $\text{K}^+$  and  $\text{NO}_3^-$ , as well as covalent between the nitrogen and oxygen atoms in  $\text{NO}_3^-$ .

### *Example 1: Electronegativity and Bond Polarity*

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 7.6, 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  $\Delta^+$  and  $\Delta^-$ :

C-H, C-N, C-O, N-H, O-H, S-H

Show Answer

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the  $\Delta^-$  designation is the more electronegative of the two. Table 1 shows these bonds in order of increasing polarity.

**Table 1. Bond Polarity and Electronegativity Difference**

Bond	$\Delta\text{EN}$	Polarity
C-H	0.4	$\begin{array}{c} \delta^- \quad \delta^+ \\ \text{C} - \text{H} \end{array}$
S-H	0.4	$\begin{array}{c} \delta^- \quad \delta^+ \\ \text{S} - \text{H} \end{array}$
C-N	0.5	$\begin{array}{c} \delta^+ \quad \delta^- \\ \text{C} - \text{N} \end{array}$
N-H	0.9	$\begin{array}{c} \delta^- \quad \delta^+ \\ \text{N} - \text{H} \end{array}$
C-O	1.0	$\begin{array}{c} \delta^+ \quad \delta^- \\ \text{C} - \text{O} \end{array}$
O-H	1.4	$\begin{array}{c} \delta^- \quad \delta^+ \\ \text{O} - \text{H} \end{array}$

### Check Your Learning

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 3, arrange the bonds in order of increasing polarity and

designate the positive and negative atoms using the symbols  $\Delta^+$  and  $\Delta^-$ .

Show Answer

Bond	Electronegativity Difference	Polarity
C-C	0.0	nonpolar
C-H	0.4	$\delta^- \text{ C} - \text{ H } \delta^+$
Si-C	0.7	$\delta^+ \text{ Si} - \text{ C } \delta^-$
Si-O	1.7	$\delta^+ \text{ Si} - \text{ O } \delta^-$

## Key Concepts and Summary

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.

## *Exercises*

1. Why is it incorrect to speak of a molecule of solid NaCl?
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.  $\text{Cl}_2\text{CO}$
  - b.  $\text{MnO}$
  - c.  $\text{NCl}_3$
  - d.  $\text{CoBr}_2$
  - e.  $\text{K}_2\text{S}$
  - f.  $\text{CO}$
  - g.  $\text{CaF}_2$
  - h.  $\text{HI}$
  - i.  $\text{CaO}$
  - j.  $\text{IBr}$
  - k.  $\text{CO}_2$
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
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
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?
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
12. Which of the following molecules or ions contain polar bonds?
- a. O<sub>3</sub>
  - b. S<sub>8</sub>
  - c. O<sub>2</sub><sup>2-</sup>
  - d. NO<sub>3</sub><sup>-</sup> (e) CO<sub>2</sub> (f) H<sub>2</sub>S (g) BH<sub>4</sub><sup>-</sup>

Selected Answers



1. NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

3. Options (b), (d), (e), (g), and (i) are ionic; Options (a), (c), (f), (h), (j), and (k) are covalent.

5. The more electronegative atoms are as follows:

- a. Cl
- b. O
- c. O
- d. S
- e. N
- f. P
- g. N

7. The correct organization of atoms, in order of increasing electronegativity, is as follows:

- 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. N, O, F, and Cl

11. The more polar bonds are as follows:

- a. HF
- b. CO
- c. OH
- d. PCl
- e. NH
- f. PO
- g. CN

## Glossary

**bond length:** distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

**covalent bond:** bond formed when electrons are shared between atoms

**electronegativity:** tendency of an atom to attract electrons in a bond to itself

**polar covalent bond:** covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

**pure covalent bond:** (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

## 32. 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:



Figure 1 shows the Lewis symbols for the elements of the third period 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	$[\text{Ne}]3s^2 3p^1$	$\cdot \overset{\cdot}{\underset{\cdot}{\text{Al}}} \cdot$
silicon	$[\text{Ne}]3s^2 3p^2$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Si}}}} \cdot$
phosphorus	$[\text{Ne}]3s^2 3p^3$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{P}}}}} \cdot$
sulfur	$[\text{Ne}]3s^2 3p^4$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{S}}}}} \cdot$
chlorine	$[\text{Ne}]3s^2 3p^5$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Cl}}}}} \cdot$
argon	$[\text{Ne}]3s^2 3p^6$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ar}}}}}}} :$

Figure 1. Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown below for chlorine and sulfur:



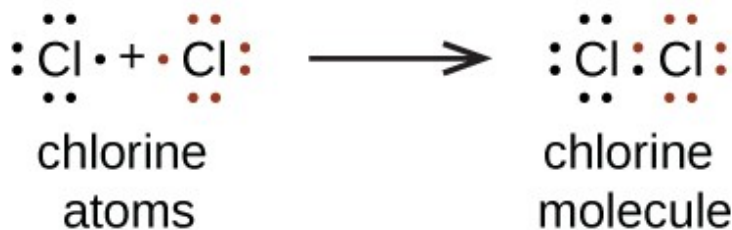
Figure 2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
$\text{Na} \cdot$ sodium atom	+	$:\ddot{\text{Cl}} \cdot$ chlorine atom	$\longrightarrow$	$\text{Na}^+ \left[ :\ddot{\text{Cl}}: \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot \text{Mg} \cdot$ magnesium atom	+	$:\ddot{\text{O}} \cdot$ oxygen atom	$\longrightarrow$	$\text{Mg}^{2+} \left[ :\ddot{\text{O}}: \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot \text{Ca} \cdot$ calcium atom	+	$2 :\ddot{\text{F}} \cdot$ fluorine atoms	$\longrightarrow$	$\text{Ca}^{2+} \left[ :\ddot{\text{F}}: \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

Figure 2. 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.

## 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:



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:

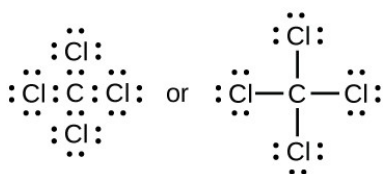


A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

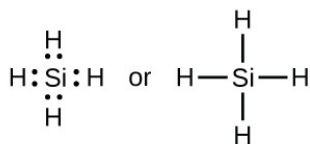
## The Octet Rule

The other halogen molecules ( $\text{F}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , and  $\text{At}_2$ ) 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  $\text{CCl}_4$  (carbon tetrachloride) and silicon in  $\text{SiH}_4$  (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:

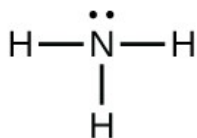


carbon tetrachloride

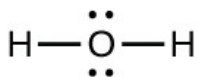


silane

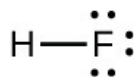
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in  $\text{NH}_3$  (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia



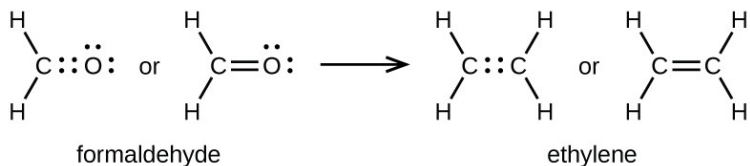
Water



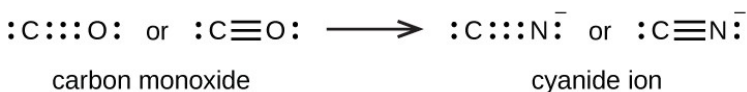
hydrogen  
fluoride

## 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  $\text{CH}_2\text{O}$  (formaldehyde) and between the two carbon atoms in  $\text{C}_2\text{H}_4$  (ethylene):

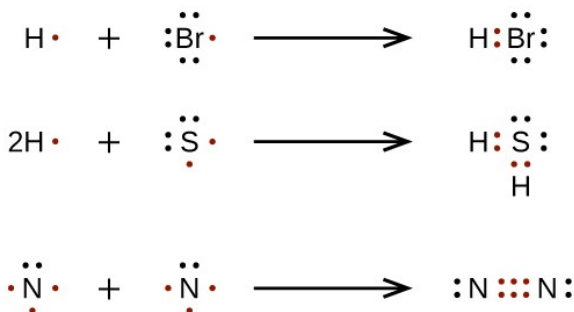


A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion ( $\text{CN}^-$ ):



## 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:



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 center.) 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  $\text{SiH}_4$ ,  $\text{CHO}_2^-$ ,  $\text{NO}^+$ , and  $\text{OF}_2$  as examples in following this procedure:

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:

$$\begin{array}{l}
 \text{SiH}_4 \\
 \text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\
 + \text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 \\
 \hline
 \phantom{+ \text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4} = 8 \text{ valence electrons}
 \end{array}$$

- For a *negative ion*, such as  $\text{CHO}_2^-$ , 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):



$$\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4$$

$$\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1$$

$$\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12$$

$$+ \quad \quad \quad 1 \text{ additional electron} = 1$$

$$= 18 \text{ valence electrons}$$

- For a *positive ion*, such as  $\text{NO}^+$ , 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:



$$\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5$$

$$\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6$$

$$+ -1 \text{ electron (positive charge)} = -1$$

$$= 10 \text{ valence electrons}$$

- Since  $\text{OF}_2$  is a neutral molecule, we simply add the number of valence electrons:



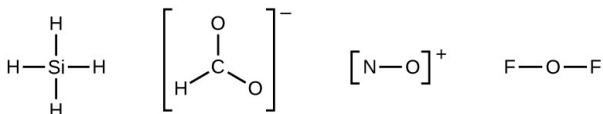
$$\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6$$

$$+ \text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14$$

$$= 20 \text{ valence electrons}$$

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

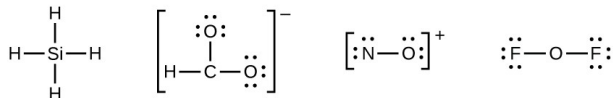
denote ions with brackets around the structure, indicating the charge outside the brackets;)



When several arrangements of atoms are possible, as for  $\text{CHO}_2^-$ , we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In  $\text{CHO}_2^-$ , the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in  $\text{POCl}_3$ , S in  $\text{SO}_2$ , and Cl in  $\text{ClO}_4^-$ . An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

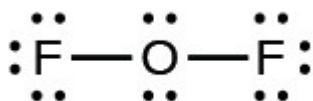
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- There are no remaining electrons on  $\text{SiH}_4$ , so it is unchanged:



4. Place all remaining electrons on the central atom.

- For  $\text{SiH}_4$ ,  $\text{CHO}_2^-$ , and  $\text{NO}^+$ , there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For  $\text{OF}_2$ , we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

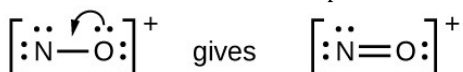


5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

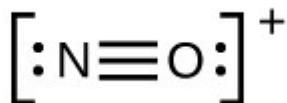
- $\text{SiH}_4$ : Si already has an octet, so nothing needs to be done.
- $\text{CHO}_2^-$ : We have distributed the valence electrons as lone pairs on the oxygen atoms, but one oxygen atom and one carbon atom lack octets:



- $\text{NO}^+$ : 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:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In  $\text{OF}_2$ , each atom has an octet as drawn, so nothing changes.

## Example 1: 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 ( $\text{H}_3\text{CCH}_3$ ), acetylene ( $\text{HCCH}$ ), and ammonia ( $\text{NH}_3$ ). What are the Lewis structures of these molecules?

Show Answer

**Step 1:** Calculate the number of valence electrons.

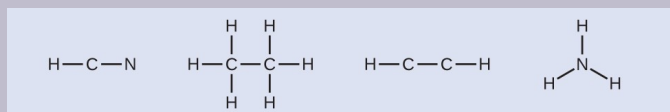
$$\text{HCN: } (1 \times 1) + (4 \times 1) + (5 \times 1) = 10$$

$$\text{H}_3\text{CCH}_3: (1 \times 3) + (2 \times 4) + (1 \times 3) = 14$$

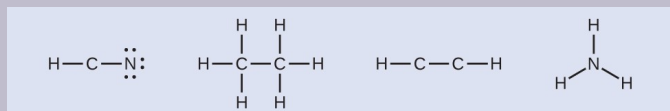
$$\text{HCCH: } (1 \times 1) + (2 \times 4) + (1 \times 1) = 10$$

$$\text{NH}_3: (5 \times 1) + (3 \times 1) = 8$$

**Step 2.** Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



**Step 3:** Where needed, distribute electrons to the terminal atoms:



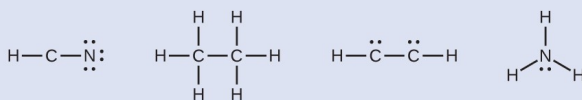
HCN: six electrons placed on N

$\text{H}_3\text{CCH}_3$ : no electrons remain

HCCH: no terminal atoms capable of accepting electrons

$\text{NH}_3$ : no terminal atoms capable of accepting electrons

**Step 4:** Where needed, place remaining electrons on the central atom:



HCN: no electrons remain

H<sub>3</sub>CCH<sub>3</sub>: no electrons remain

HCCH: four electrons placed on carbon

NH<sub>3</sub>: two electrons placed on nitrogen

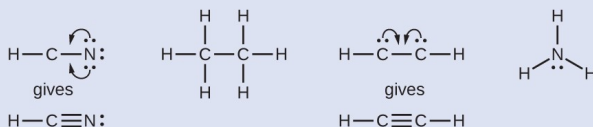
**Step 5:** Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

HCN: form two more C-N bonds

H<sub>3</sub>CCH<sub>3</sub>: all atoms have the correct number of electrons

HCCH: form a triple bond between the two carbon atoms

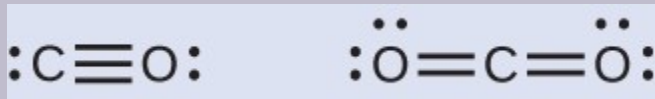
NH<sub>3</sub>: all atoms have the correct number of electrons



## Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO<sub>2</sub> has been implicated in global climate change. What are the Lewis structures of these two molecules?

Show Answer



## Fullerene Chemistry

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 3), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the  $\text{C}_{60}$  buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on  $\text{C}_{60}$ . 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

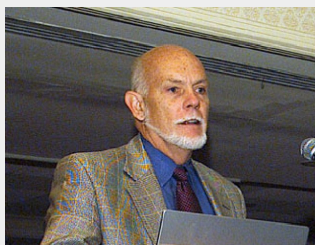


Figure 3. Richard Smalley (1943–2005). (credit: United States Department of Energy)

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, 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 U.S. Senate honored him as the “Father of Nanotechnology.”

## 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.

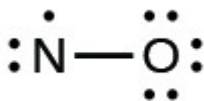
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same six steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons.*

The sum of the valence electrons is 5 (from N) + 6 (from O) = 11.

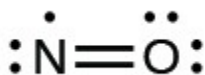
The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.

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



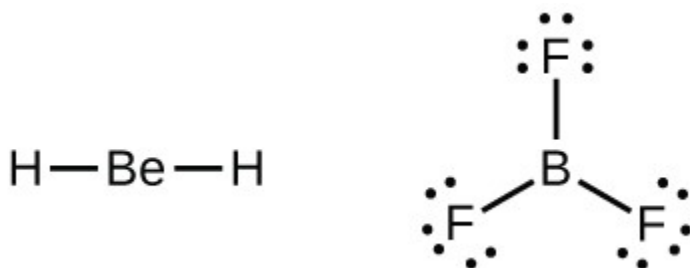
has the filled valence shell:

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;)

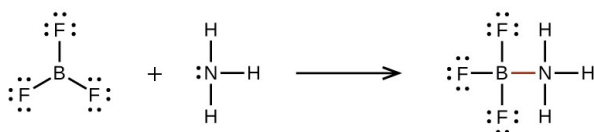


## Electron-deficient Molecules

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,  $\text{BeH}_2$ , and boron trifluoride,  $\text{BF}_3$ , 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  $\text{BF}_3$ , 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.



An atom like the boron atom in  $\text{BF}_3$ , 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,  $\text{NH}_3$  reacts with  $\text{BF}_3$  because the lone pair on nitrogen can be shared with the boron atom:



## 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 2s and three 2p 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 4 shows the Lewis structures for two hypervalent molecules, PCl<sub>5</sub> and SF<sub>6</sub>.

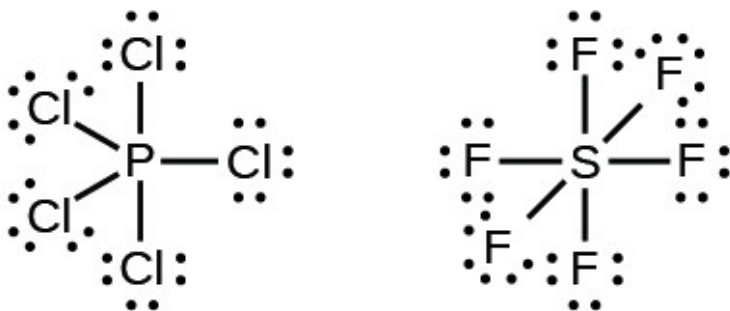
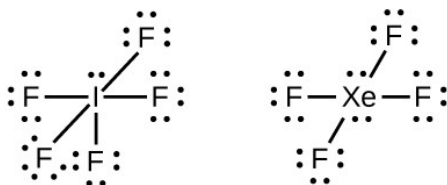


Figure 4. In PCl<sub>5</sub>, the central atom phosphorus shares five pairs of electrons. In SF<sub>6</sub>, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF<sub>5</sub> and XeF<sub>4</sub>, some of the electrons in the outer shell of the central atom are lone pairs:



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 2: Writing Lewis Structures: Octet Rule Violations*

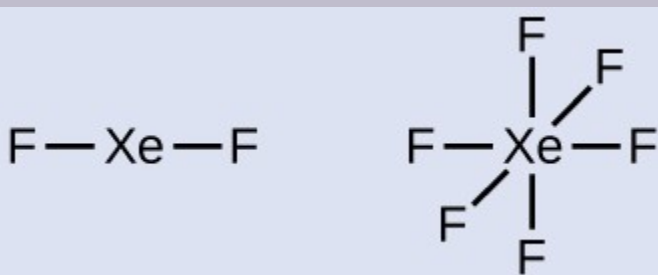
Xenon is a noble gas, but it forms a number of stable compounds. We examined  $\text{XeF}_4$  earlier. What are the Lewis structures of  $\text{XeF}_2$  and  $\text{XeF}_6$ ?

Show Answer

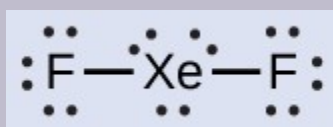
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

1. Calculate the number of valence electrons:  $\text{XeF}_2$ :  $8 + (2 \times 7) = 22$   
 $\text{XeF}_6$ :  $8 + (6 \times 7) = 50$

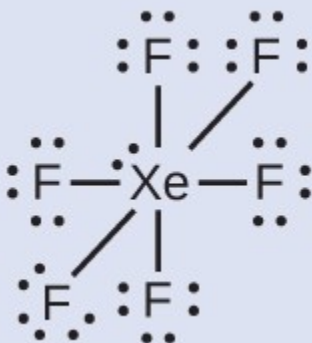
2. Draw a skeleton joining the atoms by single bonds.  
 Xenon will be the central atom because fluorine cannot be a central atom:



3. *Distribute the remaining electrons.*  $\text{XeF}_2$ : 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  $\text{XeF}_2$  shows two bonding pairs and three lone pairs of electrons around the Xe atom:



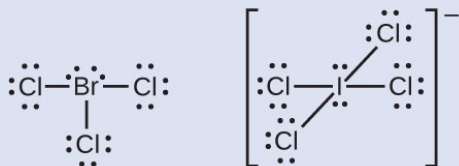
4.  $\text{XeF}_6$ : We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



### Check Your Learning

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  $\text{BrCl}_3$  and  $\text{ICl}_4^-$ .

Show Answer



## *Key Concepts and Summary*

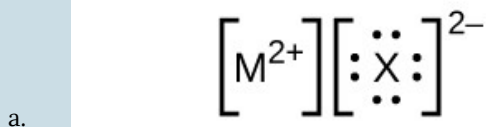
Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each 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.

## *Exercises*

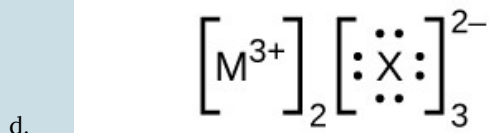
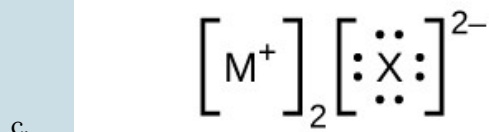
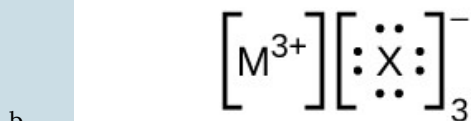
- Write the Lewis symbols for each of the following ions:
  - $\text{As}^{3-}$
  - $\text{I}^-$
  - $\text{Be}^{2+}$
  - $\text{O}^{2-}$
  - $\text{Ga}^{3+}$
  - $\text{Li}^+$
  - $\text{N}^{3-}$
- Many monatomic ions are found in seawater,

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.  $\text{Al}_2\text{O}_3$
  - c.  $\text{GaCl}_3$
  - d.  $\text{K}_2\text{O}$
  - e.  $\text{Li}_3\text{N}$
  - f. KF
4. In the Lewis structures listed below, 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:







5. Write the Lewis structure for the diatomic molecule  $P_2$ , an unstable form of phosphorus found in high-temperature phosphorus vapor.
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.  $\text{AsF}_3$
- d.  $\text{ClNO}$
- e.  $\text{SiCl}_4$
- f.  $\text{H}_3\text{O}^+$
- g.  $\text{NH}_4^+$
- h.  $\text{BF}_4^-$
- i.  $\text{HCCH}$
- j.  $\text{ClCN}$
- k.  $\text{C}_2^{2+}$

8. Write Lewis structures for the following:

- a.  $\text{ClF}_3$
- b.  $\text{PCl}_5$
- c.  $\text{BF}_3$
- d.  $\text{PF}_6^-$

9. Write Lewis structures for the following:

- a.  $\text{SeF}_6$
- b.  $\text{XeF}_4$
- c.  $\text{SeCl}_3^+$
- d.  $\text{Cl}_2\text{BBCl}_2$  (contains a B-B bond)

10. Write Lewis structures for:

- a.  $\text{PO}_4^{3-}$
- b.  $\text{ICl}_4^-$
- c.  $\text{SO}_3^{2-}$
- d.  $\text{HONO}$

11. Correct the following statement: "The bonds in solid  $\text{PbCl}_2$  are ionic; the bond in a  $\text{HCl}$  molecule is covalent. Thus, all of the valence electrons in  $\text{PbCl}_2$

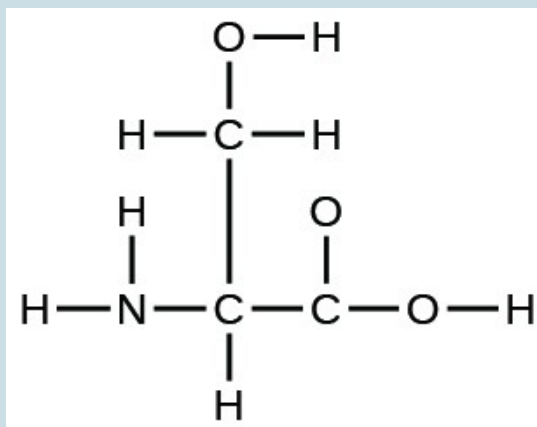
are located on the  $\text{Cl}^-$  ions, and all of the valence electrons in a  $\text{HCl}$  molecule are shared between the H and Cl atoms.”

12. Write Lewis structures for the following molecules or ions:
  - a.  $\text{SbH}_3$
  - b.  $\text{XeF}_2$
  - c.  $\text{Se}_8$  (a cyclic molecule with a ring of eight Se atoms)
13. Methanol,  $\text{H}_3\text{COH}$ , is used as the fuel in some race cars. Ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is used extensively as motor fuel in Brazil. Both methanol and ethanol produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$  when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.
14. Many planets in our solar system contain organic chemicals including methane ( $\text{CH}_4$ ) and traces of ethylene ( $\text{C}_2\text{H}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propyne ( $\text{H}_3\text{CCCH}$ ), and diacetylene ( $\text{HCCCCCH}$ ). 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,  $\text{Cl}_2\text{CO}$ . Write the Lewis structures for carbon tetrachloride and phosgene.
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.  $1s^2 2s^2 2p^5$

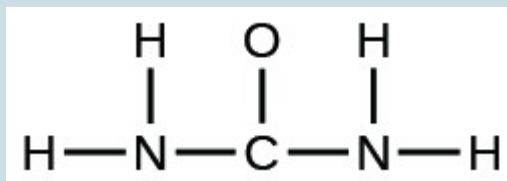
- b.  $1s^2 2s^2 2p^6 3s^2$
- c.  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
- d.  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
- e.  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

17. The arrangement of atoms in several biologically important molecules is given below. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

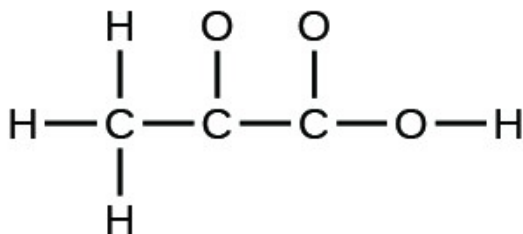
- a. the amino acid serine:



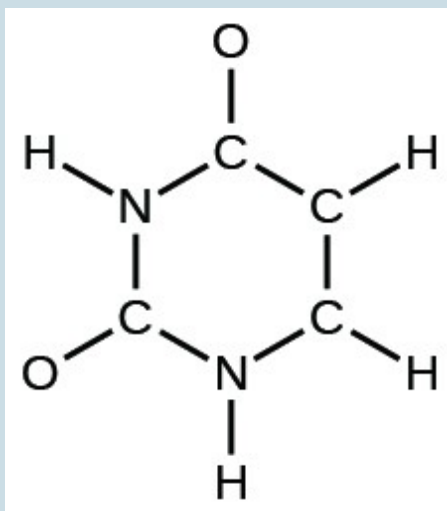
- b. urea:



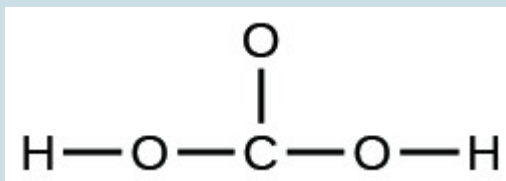
- c. pyruvic acid:



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

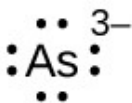
compound.

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.
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?

#### Selected Answers

1. The Lewis symbol for each ion is as follows:

- a. eight electrons:

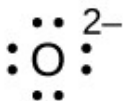


- b. eight electrons:



- c. no electrons  $\text{Be}^{2+}$

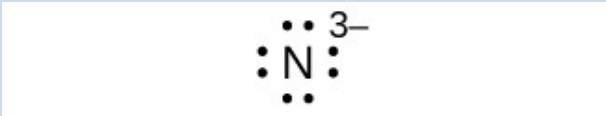
- d. eight electrons:



- e. no electrons  $\text{Ga}^{3+}$

- f. no electrons  $\text{Li}^+$

- g. eight electrons:

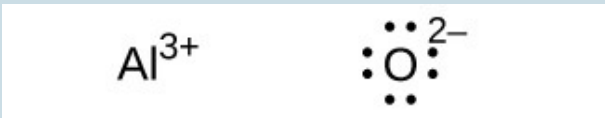


3. The Lewis symbols are as follows:

a.



b.



c.



d.



e.



f.

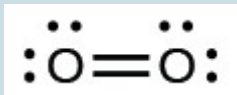


5.



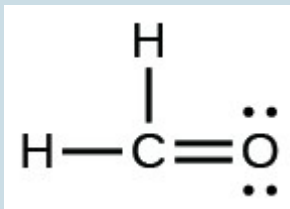
7. The Lewis structures are as follows:

- a.  $\text{O}_2$ :

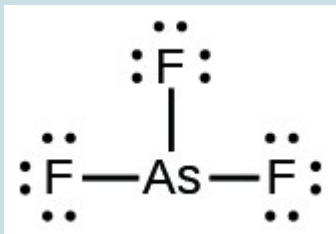


In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

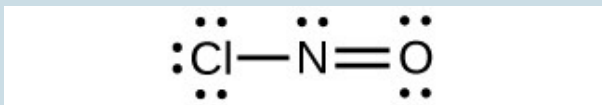
- b.  $\text{H}_2\text{CO}$ :



- c.  $\text{AsF}_3$ :

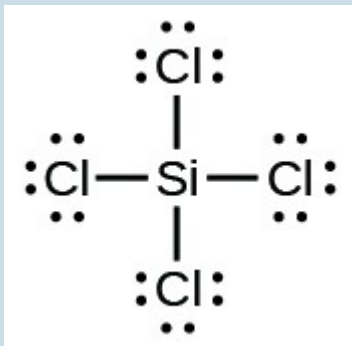


- d.  $\text{ClNO}$ :

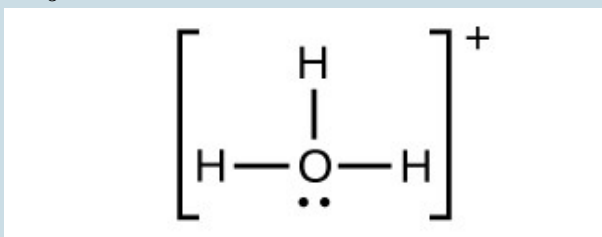


- e.  $\text{SiCl}_4$ :

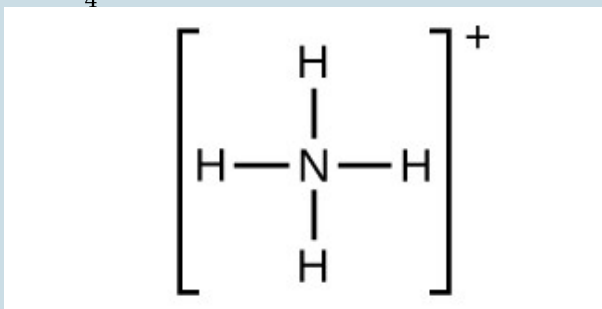




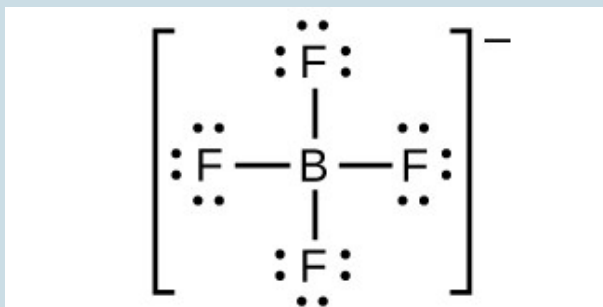
f.  $\text{H}_3\text{O}^+$ :



g.  $\text{NH}_4^+$ :



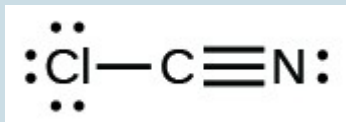
h.  $\text{BF}_4^-$ :



i. HCCH:



j. ClCN:

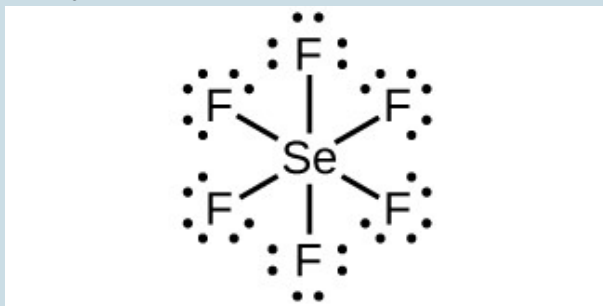


k.  $\text{C}_2^{2+}$

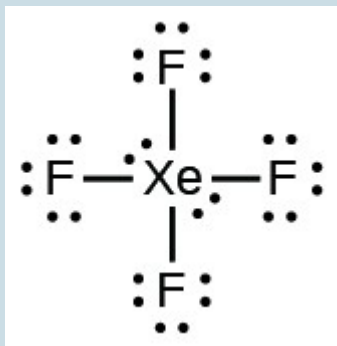


9. The Lewis structures are as follows:

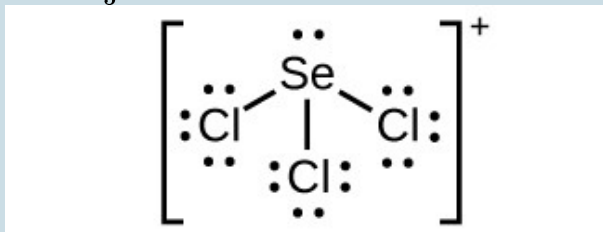
a.  $\text{SeF}_6$ :



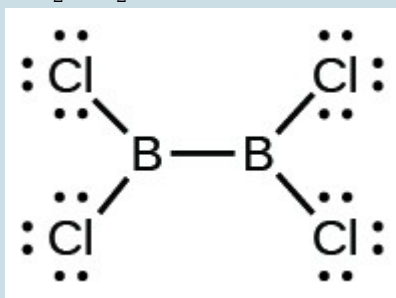
b.  $\text{XeF}_4$ :



c.  $\text{SeCl}_3^+$  :



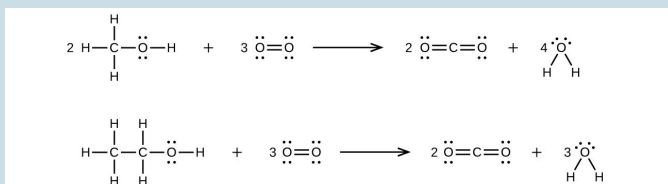
d.  $\text{Cl}_2\text{BBCl}_2$ :



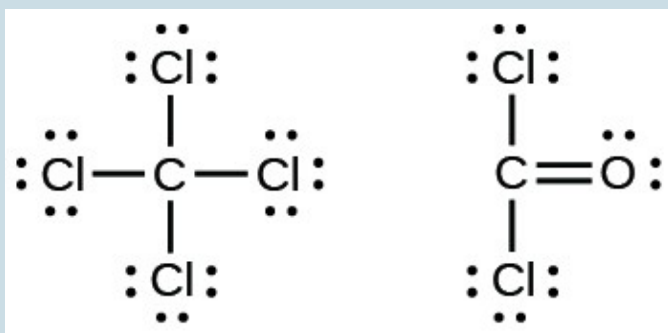
11. Two valence electrons per Pb atom are transferred to Cl atoms; the resulting  $\text{Pb}^{2+}$  ion has a  $6s^2$  valence shell configuration. Two of the valence electrons in the HCl

molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

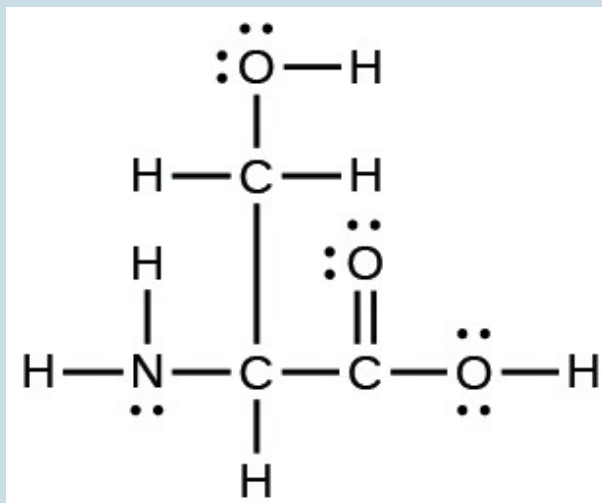
13.



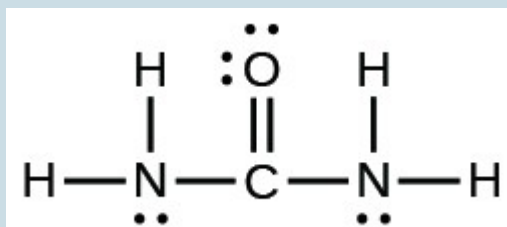
15.



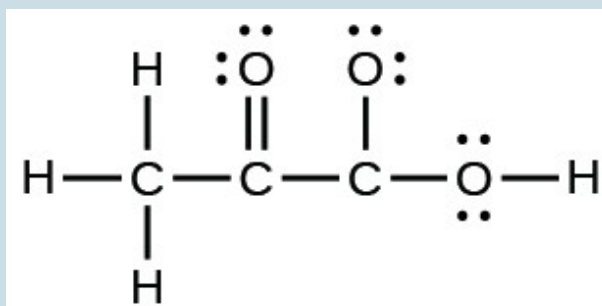
17. The completed Lewis structures are as follows:



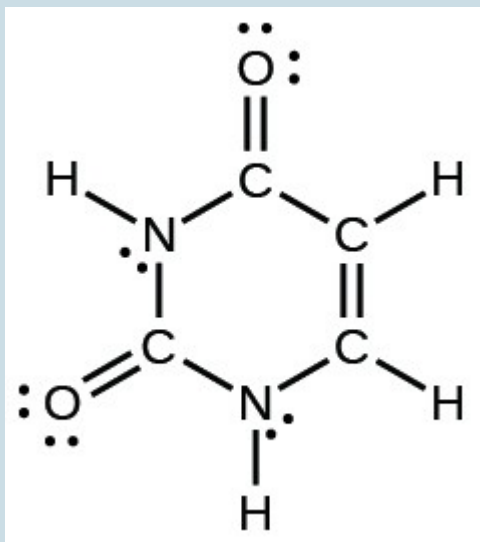
a.



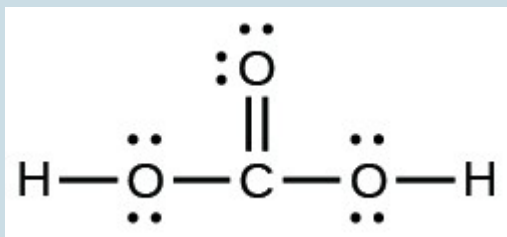
b.



c.



d.



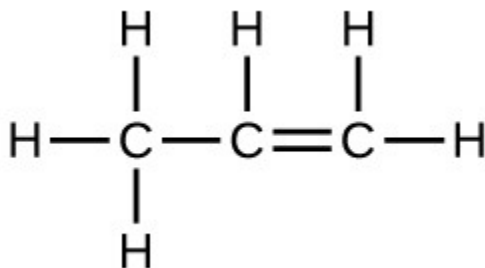
e.

19. A 100.0-g sample of this compound would contain 85.7 g C and 14.3 g H:

$$\frac{85.7\text{g}}{12.011\text{g mol}^{-1}} = 7.14\text{mol C}$$

$$\frac{14.3\text{g}}{1.00794\text{g mol}^{-1}} = 14.19\text{mol H}$$

This is a ratio of 2 H to 1 C, or an empirical formula of  $\text{CH}_2$  with a formula mass of approximately 14. As  $\frac{42}{14} = 3$ , the formula is  $3 \times \text{CH}_2$  or  $\text{C}_3\text{H}_6$ . The Lewis structure is:



21. 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.

## Glossary

**double bond:** covalent bond in which two pairs of electrons are shared between two atoms

**free radical:** molecule that contains an odd number of electrons

**hypervalent molecule:** molecule containing at least one main group element that has more than eight electrons in its valence shell

**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

**lone pair:** two (a pair of) valence electrons that are not used to form a covalent bond

**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

**single bond:** bond in which a single pair of electrons is shared between two atoms

**triple bond:** bond in which three pairs of electrons are shared between two atoms



# 33. 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, 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 1). 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 ( $1 \text{ Å} = 10^{-10} \text{ m}$ ) or picometers ( $1 \text{ pm} = 10^{-12} \text{ m}$ ,  $100 \text{ pm} = 1 \text{ Å}$ ).

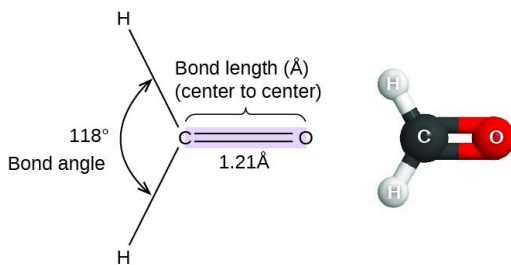


Figure 1. Bond distances (lengths) and angles are shown for the formaldehyde molecule, H<sub>2</sub>CO.

## VSEPR Theory

**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  $\text{BeF}_2$  molecule. The Lewis structure of  $\text{BeF}_2$  (Figure 2) shows only two electron pairs around the central beryllium atom. With

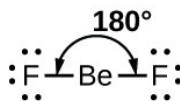


Figure 2. The  $\text{BeF}_2$  molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

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  $180^\circ$  (Figure 2). Figure 3 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.

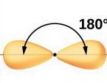
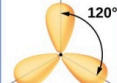
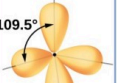
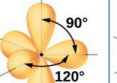
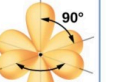




Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	$\text{H}-\text{Be}-\text{H}$				
Electron pair geometry	Linear; $180^\circ$ angle	Trigonal planar; all angles $120^\circ$	Tetrahedral; all angles $109.5^\circ$	Trigonal bipyramidal; angles of $90^\circ$ or $120^\circ$ 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 $90^\circ$ or $180^\circ$

Figure 3. The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

## 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 3 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.

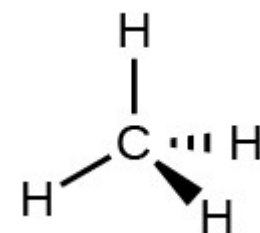


Figure 4. The molecular structure of the methane molecule,  $\text{CH}_4$ , is shown with a tetrahedral arrangement of the hydrogen atoms.

VSEPR structures like the one in Figure 4 are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane. For example, the methane molecule,  $\text{CH}_4$ , 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 4). On the other hand, the ammonia molecule,  $\text{NH}_3$ , 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 5).

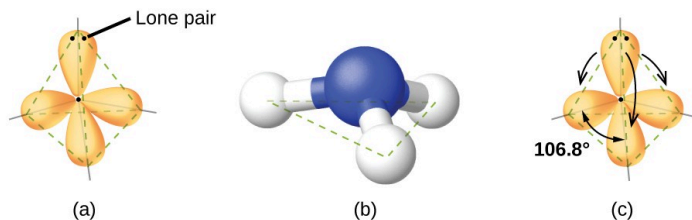


Figure 5. (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles, because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than  $109.5^\circ$ .

As seen in Figure 5, small distortions from the ideal angles in Figure 6 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:

lone pair-lone pair > lone pair-bonding pair > 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:

lone pair > triple bond > double bond > single bond

Consider formaldehyde,  $\text{H}_2\text{CO}$ , which is used as a preservative for biological and anatomical specimens (Figure 1). 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  $120^\circ$  bond angles, but we see that the double bond causes slightly larger angles ( $121^\circ$ ), and the angle between the single bonds is slightly smaller ( $118^\circ$ ).

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 5) 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  $\text{NH}_3$  are slightly smaller than the  $109.5^\circ$  angle in a regular tetrahedron (Figure 3) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 5). Figure 6 illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.







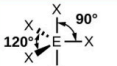
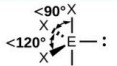
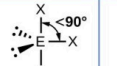
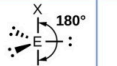

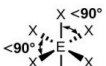



Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 6. The molecular structures are identical to the electron-pair geometries when there are 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.

According to VSEPR theory, the terminal atom locations (Xs in Figure 6) 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 7: 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 6, the axial position is



surrounded by bond angles of  $90^\circ$ , whereas the equatorial position has more space available because of the  $120^\circ$  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  $\text{ClF}_3$  molecule (Figure 7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

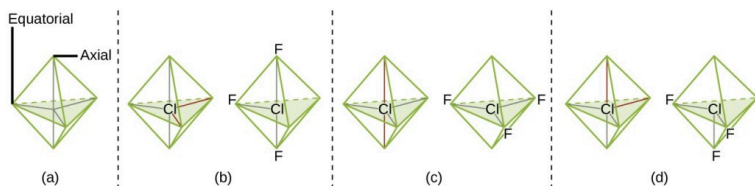


Figure 7. (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in  $\text{ClF}_3$  have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

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 ( $180^\circ$  apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 6).

## 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 6, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 6). 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 1: Predicting Electron-pair Geometry and Molecular Structure: $\text{CO}_2$ and $\text{BCl}_3$*

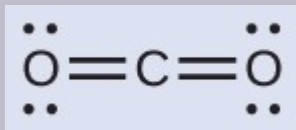
Predict the electron-pair geometry and molecular structure for each of the following:

1. carbon dioxide,  $\text{CO}_2$ , a molecule produced by the combustion of fossil fuels
2. boron trichloride,  $\text{BCl}_3$ , an important industrial

chemical

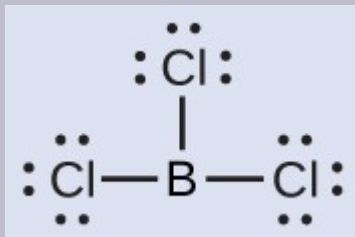
Show Answer

1. We write the Lewis structure of  $\text{CO}_2$  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  $180^\circ$ . The electron-pair geometry and molecular structure are identical, and  $\text{CO}_2$  molecules are linear.

2. We write the Lewis structure of  $\text{BCl}_3$  as:



Thus we see that  $\text{BCl}_3$  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  $\text{B-Cl}$  bonds lie in a plane with  $120^\circ$  angles between them.  $\text{BCl}_3$  also has a trigonal planar molecular structure (Figure 8).

Figure 8 shows the electron-pair geometry and molecular

structure of  $\text{BCl}_3$  are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles ( $120^\circ$ ), unlike the Lewis structure shown above.

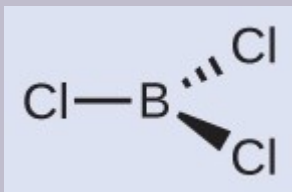


Figure 8.

### *Check Your Learning*

Carbonate,  $\text{CO}_3^{2-}$ , 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?

Show Answer

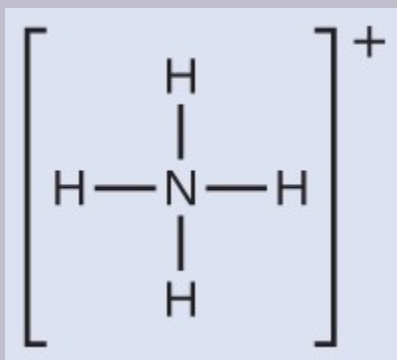
The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

## *Example 2: 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  $\text{NH}_4^+$  cation.

Show Answer

We write the Lewis structure of  $\text{NH}_4^+$  as:



We can see that  $\text{NH}_4^+$  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 6). Therefore, the electron pair geometry of  $\text{NH}_4^+$

is tetrahedral, and the molecular structure is also tetrahedral (Figure 9).

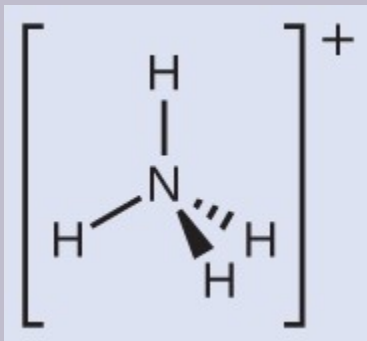


Figure 9. The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

### *Check Your Learning*

Identify a molecule with trigonal bipyramidal molecular structure.

Show Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal.  $\text{PF}_5$  is a common example.

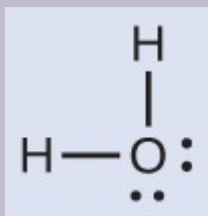
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

### *Example 3: 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.

Show Answer

The Lewis structure of  $\text{H}_2\text{O}$  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 10), as indicated in Figure 6. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than  $109.5^\circ$ . In fact, the bond angle is  $104.5^\circ$ .

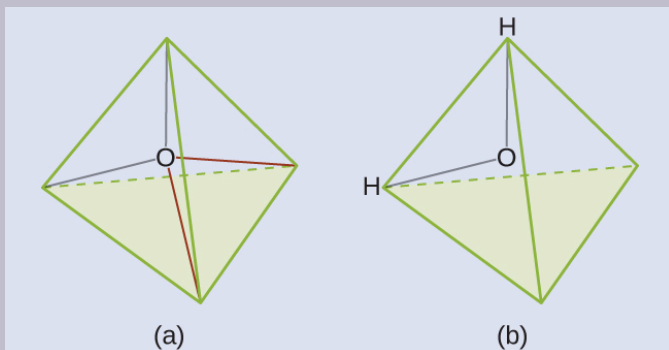


Figure 10. (a) H<sub>2</sub>O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

### Check Your Learning

The hydronium ion, H<sub>3</sub>O<sup>+</sup>, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Show Answer

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

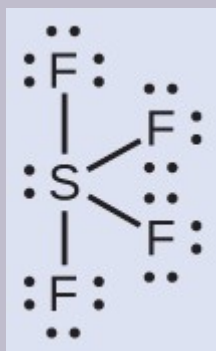


### *Example 4: Predicting Electron-pair Geometry and Molecular Structure: SF<sub>4</sub>*

Sulfur tetrafluoride, SF<sub>4</sub>, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF<sub>4</sub> is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF<sub>4</sub> molecule.

Show Answer

The Lewis structure of SF<sub>4</sub> 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) is that of a seesaw (Figure 6).

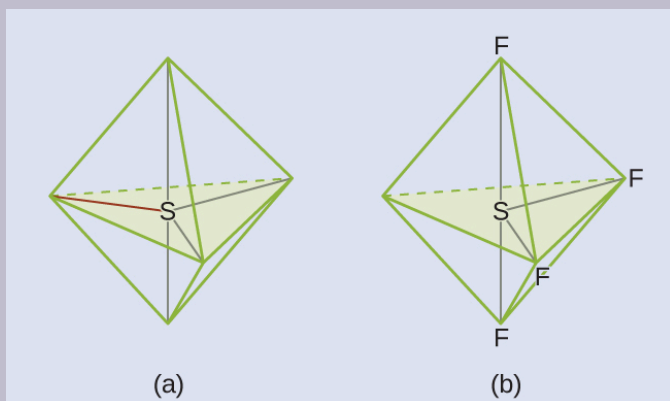


Figure 11. (a)  $\text{SF}_4$  has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

### Check Your Learning

Predict the electron pair geometry and molecular structure for molecules of  $\text{XeF}_2$ .

Show Answer

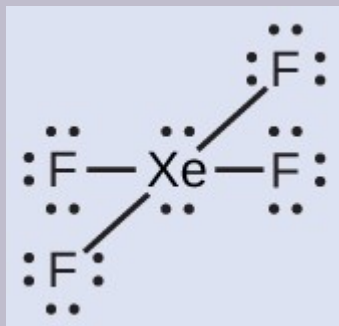
The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

### *Example 5: Predicting Electron-pair Geometry and Molecular Structure: XeF<sub>4</sub>*

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<sub>4</sub> molecule.

Show Answer

The Lewis structure of XeF<sub>4</sub> 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 6), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 12). The five atoms are all in the same plane and have a square planar molecular structure.

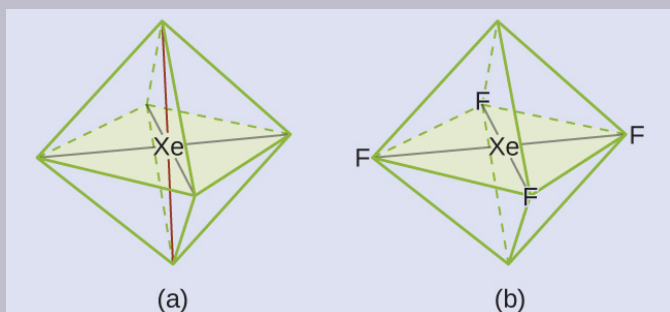


Figure 12. (a)  $\text{XeF}_4$  adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

### Check Your Learning

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Show Answer

electron pair geometry: trigonal bipyramidal; molecular structure: linear

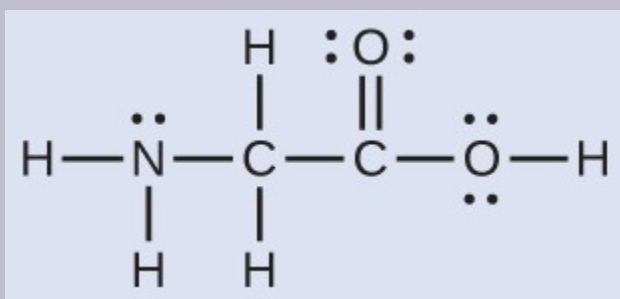
## Molecular Structure for Multicenter Molecules

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

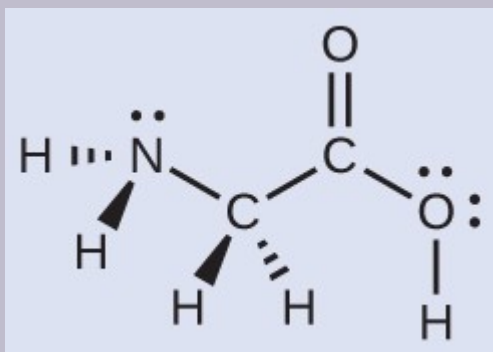
“local” geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

### *Example 6: Predicting Structure in Multicenter Molecules*

The Lewis structure for the simplest amino acid, glycine,  $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ , is shown below. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Show Answer



Consider each central atom independently. The electron-pair geometries:

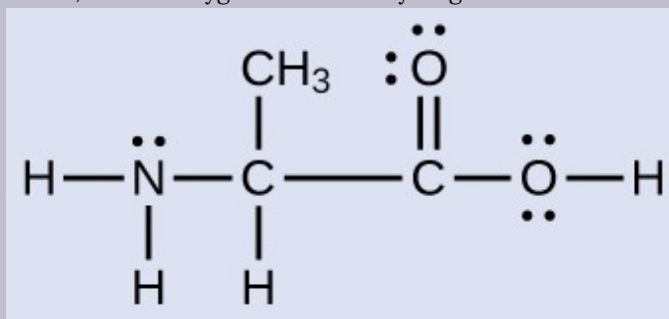
- nitrogen—four regions of electron density; tetrahedral
- carbon ( $\text{CH}_2$ )—four regions of electron density; tetrahedral
- carbon ( $\text{CO}_2$ )—three regions of electron density; trigonal planar
- oxygen ( $\text{OH}$ )—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ( $\text{CH}_2$ )—four bonds, no lone pairs; tetrahedral
- carbon ( $\text{CO}_2$ )—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ( $\text{OH}$ )—two bonds, two lone pairs; bent ( $109^\circ$ )

### Check Your Learning

Another amino acid is alanine, which has the Lewis structure shown below. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Show Answer

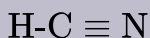
electron-pair geometries: nitrogen--tetrahedral; carbon (CH)--tetrahedral; carbon (CH<sub>3</sub>)--tetrahedral; carbon (CO<sub>2</sub>)--trigonal planar; oxygen (OH)--tetrahedral; local structures: nitrogen--trigonal pyramidal; carbon (CH)--tetrahedral; carbon (CH<sub>3</sub>)--tetrahedral; carbon (CO<sub>2</sub>)--trigonal planar; oxygen (OH)--bent (109°)

The [molecular shape simulator from PhET](#) lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

### Example 7: Molecular Simulation

Using [molecular shape simulator](#) 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:



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?

Show Answer

The molecular structure is linear.

### Check Your Learning

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.

Show Answer

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<sub>4</sub> is a molecule that adopts this structure.

## 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 ( $\Delta^+$ ) and the other atom with a partial negative charge ( $\Delta^-$ ), 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 ( $\mu$ ) and is given by the formula shown below, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude (Figure 13). 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.

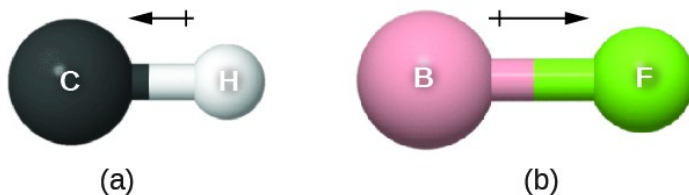


Figure 13. (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

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  $\text{Br}_2$  and  $\text{N}_2$  have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as  $\text{CO}$ , there is a small dipole moment. For  $\text{HF}$ , 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  $\text{CO}_2$  (Figure 14). 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  $\text{CO}_2$  molecule is linear with polar  $\text{C}=\text{O}$  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 14), 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).

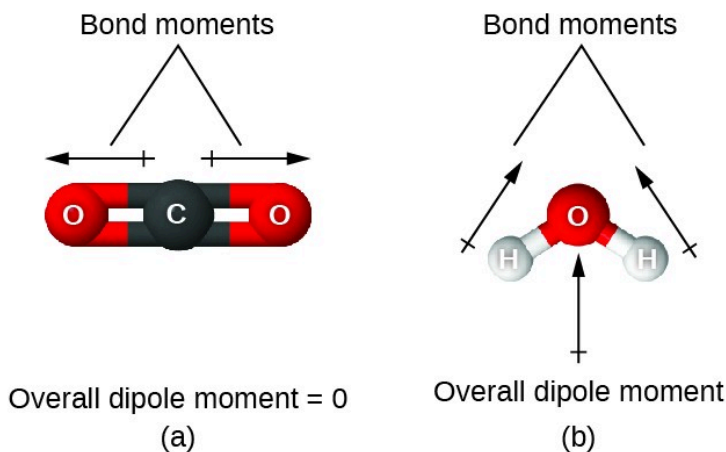
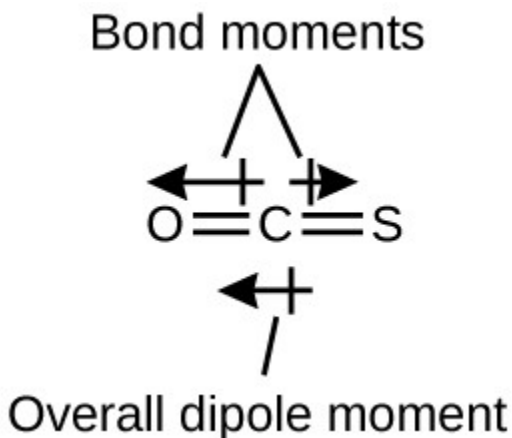


Figure 14. The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net  $\text{CO}_2$  molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to  $\text{CO}_2$ , 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:



Although the C–O bond is polar, C and S have the same electronegativity values as shown in Figure 15, so there is no C–S dipole. Thus, the two bonds do not have of the same bond dipole moment, and the bond moments do not cancel. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

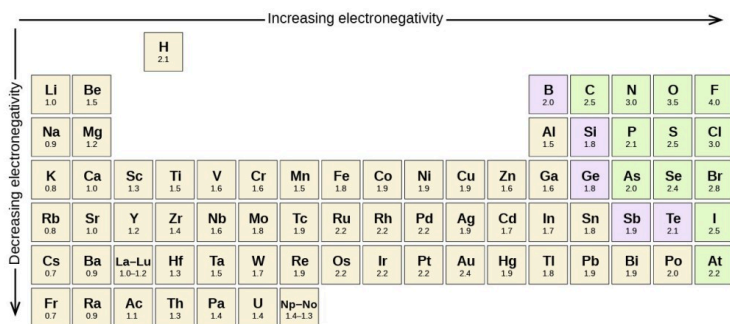
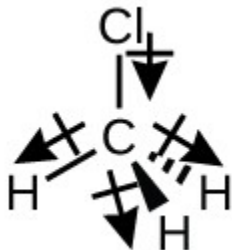
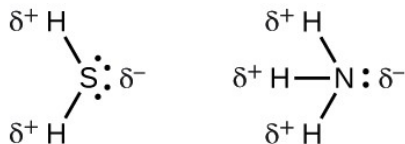


Figure 15. The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Chloromethane,  $\text{CH}_3\text{Cl}$ , is another example of a polar molecule. Although the polar  $\text{C}-\text{Cl}$  and  $\text{C}-\text{H}$  bonds are arranged in a tetrahedral geometry, the  $\text{C}-\text{Cl}$  bonds have a larger bond moment than the  $\text{C}-\text{H}$  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:



When we examine the highly symmetrical molecules  $\text{BF}_3$  (trigonal planar),  $\text{CH}_4$  (tetrahedral),  $\text{PF}_5$  (trigonal bipyramidal), and  $\text{SF}_6$  (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  $\text{H}_2\text{S}$  and  $\text{NH}_3$ . 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:



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.

## 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 (Figure 16). 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.

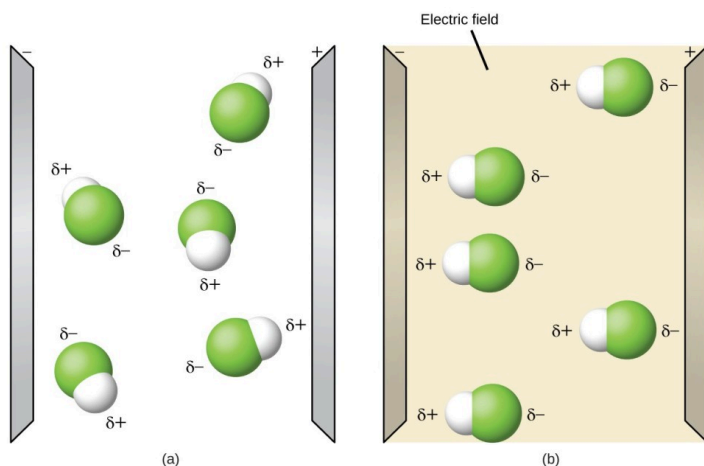


Figure 16. (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

The [PhET molecule polarity simulation](#) provides many ways to explore dipole moments of bonds and molecules.

### *Example 8: Polarity Simulations*

Open the [PhET molecule polarity simulation](#) and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjusters. 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 15.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

1. A and C are very electronegative and B is in the middle of the range.
2. A is very electronegative, and B and C are not.

Show Answer

1. Molecular dipole moment points immediately between A and C.
2. Molecular dipole moment points along the A–B bond, toward A.

## *Check Your Learning*

Determine the partial charges that will give the largest possible bond dipoles.

Show Answer

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.

## *Key Concepts and Summary*

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.

## *Exercises*

1. Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.
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.
4. Why is the H-N-H angle in  $\text{NH}_3$  smaller than the H-C-H bond angle in  $\text{CH}_4$ ? Why is the H-N-H angle in  $\text{NH}_4^+$  identical to the H-C-H bond angle in  $\text{CH}_4$ ?
5. Explain how a molecule that contains polar bonds can be nonpolar.
6. As a general rule,  $\text{MX}_n$  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.  $\text{NH}_3$  (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.  $\text{SF}_6$
- b.  $\text{PCl}_5$
- c.  $\text{BeH}_2$
- d.  $\text{CH}_3^+$

8. Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

- a.  $\text{IF}_6^+$
- b.  $\text{CF}_4$
- c.  $\text{BF}_3$
- d.  $\text{SiF}_5^-$
- e.  $\text{BeCl}_2$

9. What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

- a.  $\text{ClF}_5$
- b.  $\text{ClO}_2^-$
- c.  $\text{TeCl}_4^{2-}$
- d.  $\text{PCl}_3$
- e.  $\text{SeF}_4$
- f.  $\text{PH}_2^-$

10. Predict the electron pair geometry and the molecular structure of each of the following ions:

- a.  $\text{H}_3\text{O}^+$
  - b.  $\text{PCl}_4^-$
  - c.  $\text{SnCl}_3^-$
  - d.  $\text{BrCl}_4^-$
  - e.  $\text{ICl}_3$
  - f.  $\text{XeF}_4$
  - g.  $\text{SF}_2$
11. Identify the electron pair geometry and the molecular structure of each of the following molecules:
- a.  $\text{ClNO}$  (N is the central atom)
  - b.  $\text{CS}_2$
  - c.  $\text{Cl}_2\text{CO}$  (C is the central atom)
  - d.  $\text{Cl}_2\text{SO}$  (S is the central atom)
  - e.  $\text{SO}_2\text{F}_2$  (S is the central atom)
  - f.  $\text{XeO}_2\text{F}_2$  (Xe is the central atom)
  - g.  $\text{ClOF}_2^+$  (Cl is the central atom)
12. Predict the electron pair geometry and the molecular structure of each of the following:
- a.  $\text{IOF}_5$  (I is the central atom)
  - b.  $\text{POCl}_3$  (P is the central atom)
  - c.  $\text{Cl}_2\text{SeO}$  (Se is the central atom)
  - d.  $\text{ClSO}^+$  (S is the central atom)
  - e.  $\text{F}_2\text{SO}$  (S is the central atom)
  - f.  $\text{NO}_2^-$
  - g.  $\text{SiO}_4^{4-}$
13. Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have

dipole moments?

- a.  $\text{ClF}_5$
  - b.  $\text{ClO}_2^-$
  - c.  $\text{TeCl}_4^{2-}$
  - d.  $\text{PCl}_3$
  - e.  $\text{SeF}_4$
  - f.  $\text{PH}_2^-$
  - g.  $\text{XeF}_2$
14. Which of the molecules and ions in Exercise 9 contain polar bonds? Which of these molecules and ions have dipole moments?
- a.  $\text{H}_3\text{O}^+$
  - b.  $\text{PCl}_4^-$
  - c.  $\text{SnCl}_3^-$
  - d.  $\text{BrCl}_4^-$
  - e.  $\text{ICl}_3$
  - f.  $\text{XeF}_4$
  - g.  $\text{SF}_2$
15. Which of the following molecules have dipole moments?
- a.  $\text{CS}_2$
  - b.  $\text{SeS}_2$
  - c.  $\text{CCl}_2\text{F}_2$
  - d.  $\text{PCl}_3$  (P is the central atom)
  - e.  $\text{ClNO}$  (N is the central atom)
16. Identify the molecules with a dipole moment:
- a.  $\text{SF}_4$

- b.  $\text{CF}_4$
  - c.  $\text{Cl}_2\text{CCBr}_2$
  - d.  $\text{CH}_3\text{Cl}$
  - e.  $\text{H}_2\text{CO}$
17. The molecule  $\text{XF}_3$  has a dipole moment. Is X boron or phosphorus?
  18. The molecule  $\text{XCl}_2$  has a dipole moment. Is X beryllium or sulfur?
  19. Is the  $\text{Cl}_2\text{BBCl}_2$  molecule polar or nonpolar?
  20. There are three possible structures for  $\text{PCl}_2\text{F}_3$  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,  $\text{H}_2\text{SO}_4$   
 $[(\text{HO})_2\text{SO}_2]$
    - b. the chlorine atom in chloric acid,  $\text{HClO}_3$   
 $[\text{HOClO}_2]$
    - c. the oxygen atom in hydrogen peroxide,  
 $\text{HOOH}$
    - d. the nitrogen atom in nitric acid,  $\text{HNO}_3$   
 $[\text{HONO}_2]$
    - e. the oxygen atom in the OH group in nitric acid,  $\text{HNO}_3$   $[\text{HONO}_2]$
    - f. the central oxygen atom in the ozone molecule,  $\text{O}_3$
    - g. each of the carbon atoms in propyne,  
 $\text{CH}_3\text{CCH}$
    - h. the carbon atom in Freon,  $\text{CCl}_2\text{F}_2$
    - i. each of the carbon atoms in allene,  $\text{H}_2\text{CCCH}_2$

22. Draw the Lewis structures and predict the shape of each compound or ion:
- $\text{CO}_2$
  - $\text{NO}_2^-$
  - $\text{SO}_3$
  - $\text{SO}_3^{2-}$
23. A molecule with the formula  $\text{AB}_2$ , 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.
24. A molecule with the formula  $\text{AB}_3$ , 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:
- $\text{CS}_3^{2-}$
  - $\text{CS}_2$
  - $\text{CS}$
  - predict the molecular shapes for  $\text{CS}_3^{2-}$  and  $\text{CS}_2$  and explain how you arrived at your predictions
26. What is the molecular structure of the stable form of  $\text{FNO}_2$ ? (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?

28. Use the [PhET 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 [PhET 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  $\text{O}_3$ . Explain your observations.
  - b. Look at the bond dipoles for  $\text{NH}_3$ . Use these dipoles to predict whether N or H is more electronegative.
  - c. Predict whether there should be a molecular dipole for  $\text{NH}_3$  and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.
30. Use the [PhET 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.

31. Use the [PhET Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select  $\text{H}_2\text{O}$ . Switch between the “real” and “model” modes. Explain the difference observed.
32. Use the [PhET Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select “model” mode and  $\text{S}_2\text{O}$ . What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

#### Show Selected Answers

1. 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  $\text{HBeH}$  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.

3. 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.

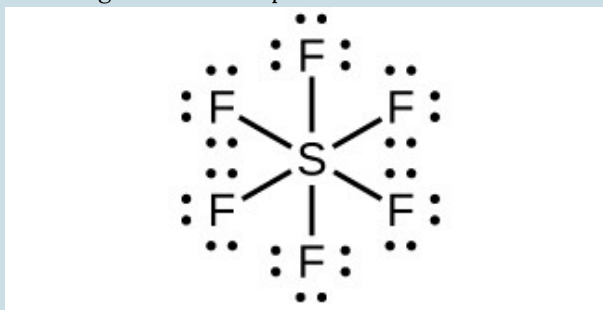
5. As long as the polar bonds are compensated (for



example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

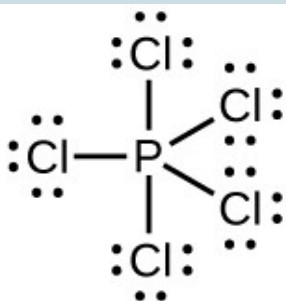
7. The electron pair geometry and the molecular structure of each are as follows:

- a. Number of valence electrons: S = 6, F = 7 each, total 48. A single line bond represents two electrons:



The total number of electrons used is 48; six bonds are formed and no nonbonded pairs exist. Therefore the molecule includes six regions of electron density and, from the table, the electron geometry is octahedral. Since no lone pairs exist, the electron geometry and molecular structure are the same.

- b. Number of valence electrons: P = 5, Cl = 7 each, total 40:



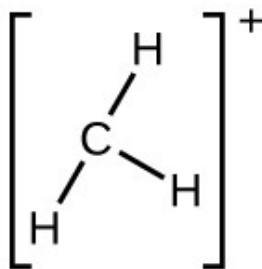
The total number of electrons is 40; there are five regions of electron density and, from the table, the geometry is trigonal bipyramid. Since no lone pairs exist on P, the electron geometry and molecular structure are the same.

- c. Number of valence electrons: Be = 2, H = 1 each, total 4:



There are only two regions of electron density and they must have a linear arrangement. These regions also correspond to the location of the bonds. Both the electron and molecular structures are linear.

- d. Number of valence electrons: C = 4, H = 1 each, less one electron because of the positive charge, for a total of six electrons:



There are three regions of electron density coincident with the three bonds. Therefore the shape is trigonal planar for both the electron geometry and molecular structure.

9. The electron pair geometry and the molecular structure of each are as follows:

- 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 bipyramidal, molecular structure: seesaw
- f. electron-pair geometry: tetrahedral, molecular structure: bent ( $109^\circ$ )

11. The electron pair geometry and the molecular structure of each are as follows:

- a. electron-pair geometry: trigonal planar, molecular

structure: bent ( $120^\circ$ )

- 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

13. All of these molecules and ions contain polar bonds. Only  $\text{ClF}_5$ ,  $\text{ClO}_2^-$ ,  $\text{PCl}_3$ ,  $\text{SeF}_4$ , and  $\text{PH}_2^-$  have dipole moments.

15. The answers are as follows:

- a.  $\text{CS}_2$  is linear and has no dipole moment.
- b.  $\text{SeS}_2$  is bent. This leads to an overall dipole moment.
- c. The C-Cl and C-F bonds are not balanced—that is, the dipoles do not completely cancel. Therefore, it has a dipole moment.
- d.  $\text{PCl}_3$  is trigonal pyramidal. Due to this shape, the dipoles of the bonds do not cancel and there is an overall dipole moment.
- e. The ClNO molecule is bent, leading to a dipole moment.

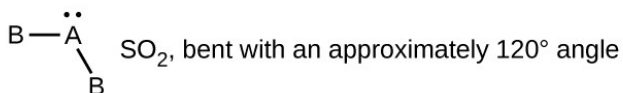
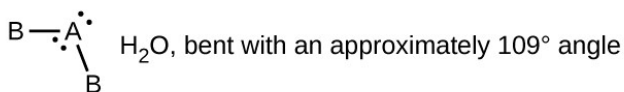
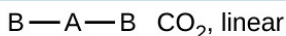
17. P

19. nonpolar

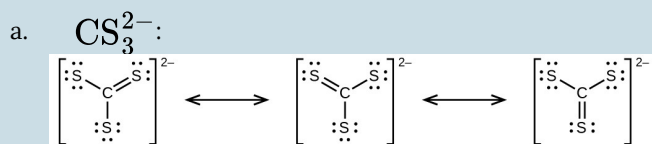
21. The molecular structures are as follows:

- a. tetrahedral
- b. trigonal pyramidal
- c. bent ( $109^\circ$ )
- d. trigonal planar
- e. bent ( $109^\circ$ )
- f. bent ( $109^\circ$ )
- g.  $\text{CH}_3\text{CCH}$  tetrahedral,  $\text{CH}_3\text{CCH}$  linear
- h. tetrahedral
- i.  $\text{H}_2\text{CCCH}_2$  linear;  $\text{H}_2\text{CCCH}_2$  trigonal planar

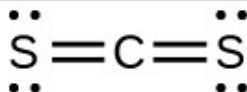
23. The three different possible shapes are



25. The Lewis electron dot structures are as follows:



b.  $\text{CS}_2$ :

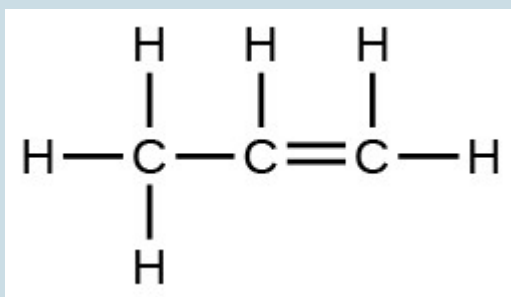


c.  $\text{CS}$ :



- d.  $\text{CS}_3^{2-}$  includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar;  $\text{CS}_2$  has only two regions of electron density (all bonds with no lone pairs); the shape is linear

27. The empirical formula is  $\text{CH}_2$  with a unit mass of 14.  
 $\frac{42}{14} = 3$ . Therefore, the Lewis structure is made from three units, but the atoms must be rearranged:



29. The molecular dipole points away from the hydrogen atoms.

31. The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as  $109.5^\circ$ . In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of  $104.5^\circ$ .

## Glossary

**axial position:** location in a trigonal bipyramidal geometry in which

there is another atom at a  $180^\circ$  angle and the equatorial positions are at a  $90^\circ$  angle

**bond angle:** angle between any two covalent bonds that share a common atom

**bond distance:** (also, bond length) distance between the nuclei of two bonded atoms

**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

**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

**electron-pair geometry:** arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

**equatorial position:** one of the three positions in a trigonal bipyramidal geometry with  $120^\circ$  angles between them; the axial positions are located at a  $90^\circ$  angle

**linear:** shape in which two outside groups are placed on opposite sides of a central atom

**molecular structure:** structure that includes only the placement of the atoms in the molecule

**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

**polar molecule:** (also, dipole) molecule with an overall dipole moment

**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  $109.5^\circ$  angles between each pair and the central atom

**trigonal bipyramidal:** shape in which five outside groups are placed around a central atom such that three form a flat triangle with  $120^\circ$  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  $120^\circ$  angles between each pair and the central atom

**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

**vector:** quantity having magnitude and direction



PART VIII

# CHEMICAL REACTIONS



## 34. 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, total ionic, and net ionic 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 ( $\text{CH}_4$ ) and two diatomic oxygen molecules ( $\text{O}_2$ ) to produce one carbon dioxide molecule ( $\text{CO}_2$ ) and two water molecules ( $\text{H}_2\text{O}$ ). The chemical equation representing this process is provided in the upper half of Figure 1, with space-filling molecular models shown in the lower half of the figure.

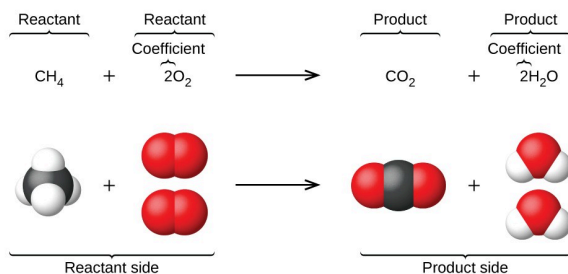


Figure 1. The reaction between methane and oxygen to yield carbon dioxide in water (shown at bottom) may be represented by a chemical equation using formulas (top).

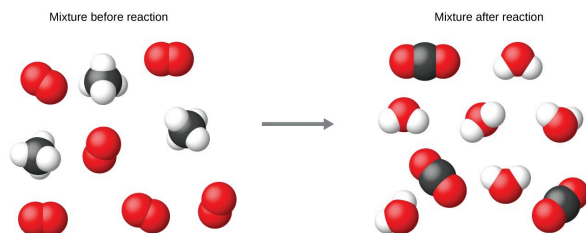
This example illustrates the fundamental aspects of any chemical equation:

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 side of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow ( $\longrightarrow$ ) 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 2). 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 2. Regardless of the absolute number of molecules involved, the ratios between numbers of molecules are the same as that given in the chemical equation.*

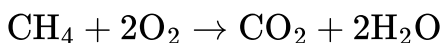
## Balancing Equations

A **balanced chemical equation** has 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,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

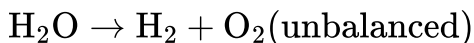
$$\left(1\text{CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}}\right) + \left(2\text{H}_2\text{O molecule} \times \frac{1 \text{ O atom}}{\text{H}_2\text{O molecule}}\right) = 4 \text{ O atoms}$$

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:



Element	Reactants	Products	Balanced?
C	$1 \times 1 = 1$	$1 \times 1 = 1$	$1 = 1$ , yes
H	$4 \times 1 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$2 \times 2 = 4$	$(1 \times 2) + (2 \times 1) = 4$	$4 = 4$ , yes

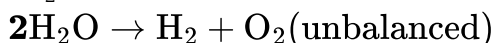
A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:



Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

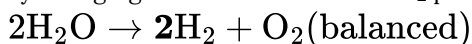
Element	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$ , no

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<sub>2</sub>O to H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O to 2.



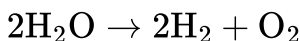
Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$4 \neq 2$ , no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H<sub>2</sub> product to 2.



Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

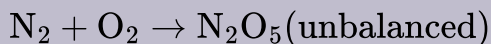


### Example 1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ) to form dinitrogen pentoxide.

Show Answer

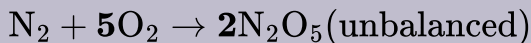
First, write the unbalanced equation:



Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes
O	$1 \times 2 = 2$	$1 \times 5 = 5$	$2 \neq 5$ , no

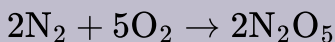
Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the  $\text{O}_2$  and  $\text{N}_2\text{O}_5$  to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).



Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$2 \times 2 = 4$	$2 \neq 4$ , no
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$ , yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant  $\text{N}_2$  to 2.





Element	Reactants	Products	Balanced?
N	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$ , yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

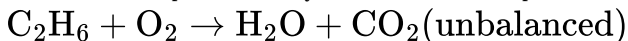
### *Check Your Learning*

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.)

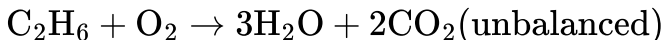
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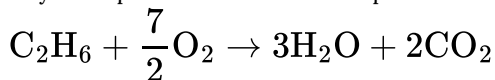
It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane ( $\text{C}_2\text{H}_6$ ) with oxygen to yield  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , represented by the unbalanced equation:



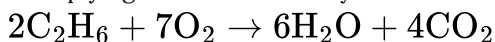
Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:



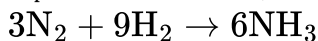
This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O<sub>2</sub> reactant to yield an odd number, so a fractional coefficient,  $\frac{7}{2}$ , is used instead to yield a provisional balanced equation:



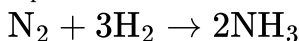
A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:



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,



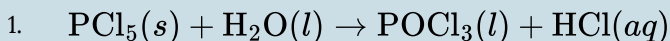
the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:



Use [this interactive PhET tutorial for additional practice balancing equations](#).

## Exercises

Balance the following equations:



2.  $\text{Ag}(s) + \text{H}_2\text{S}(g) + \text{O}_2(g) \rightarrow \text{Ag}_2\text{S}(s) + \text{H}_2\text{O}(l)$
3.  $\text{Cu}(s) + \text{HNO}_3(aq) \rightarrow \text{Cu}(\text{NO}_3)_2(aq) + \text{H}_2\text{O}(l) + \text{NO}(g)$
4.  $\text{P}_4(s) + \text{O}_2(g) \rightarrow \text{P}_4\text{O}_{10}(s)$
5.  $\text{H}_2(g) + \text{I}_2(s) \rightarrow \text{HI}(s)$
6.  $\text{Pb}(s) + \text{H}_2\text{O}(l) + \text{O}_2(g) \rightarrow \text{Pb}(\text{OH})_2(s)$
7.  $\text{Fe}(s) + \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$
8.  $\text{Fe}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Fe}_3\text{O}_4(s) + \text{H}_2(g)$
9.  $\text{Na}(s) + \text{H}_2\text{O}(l) \rightarrow \text{NaOH}(aq) + \text{H}_2(g)$
10.  $\text{Sc}_2\text{O}_3(s) + \text{SO}_3(l) \rightarrow \text{Sc}_2(\text{SO}_4)_3(s)$
11.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \rightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + \text{H}_2\text{O}(g)$
12.  $\text{Ca}_3(\text{PO}_4)_2(aq) + \text{H}_3\text{PO}_4(aq) \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2(aq)$
13.  $\text{P}_4(s) + \text{Cl}_2(g) \rightarrow \text{PCl}_3(l)$
14.  $\text{Al}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Al}_2(\text{SO}_4)_3(aq) + \text{H}_2(g)$
15.  $\text{PtCl}_4(s) \rightarrow \text{Pt}(s) + \text{Cl}_2(g)$
16.  $\text{TiCl}_4(s) + \text{H}_2\text{O}(g) \rightarrow \text{TiO}_2(s) + \text{HCl}(g)$

Show Answer

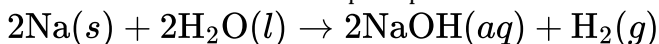
The balanced equations are as follows:

1.  
 $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \rightarrow \text{POCl}_3(l) + 2\text{HCl}(aq);$
3.  
 $3\text{Cu}(s) + 8\text{HNO}_3(aq) \rightarrow 3\text{Cu}(\text{NO}_3)_2(aq) + 4\text{H}_2\text{O}(l) + 2\text{NO}(g);$
5.  $\text{H}_2(g) + \text{I}_2(s) \rightarrow 2\text{HI}(s);$
7.  $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s);$
9.  
 $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g);$
11.  
 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \rightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + 4\text{H}_2\text{O}(g);$
13.  $\text{P}_4(s) + 6\text{Cl}_2(g) \rightarrow 4\text{PCl}_3(l);$



## 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:



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 ( $\Delta$ ) over the arrow.

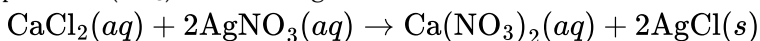


Other examples of these special conditions will be encountered in more depth in later chapters.

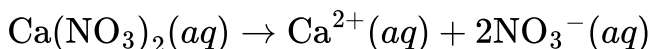
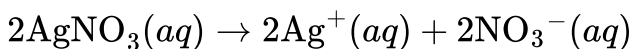
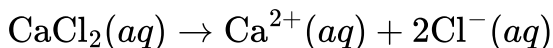
## Equations for Ionic Reactions

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  $\text{CaCl}_2$  and  $\text{AgNO}_3$  are mixed, a reaction takes place producing aqueous  $\text{Ca}(\text{NO}_3)_2$  and solid  $\text{AgCl}$ :

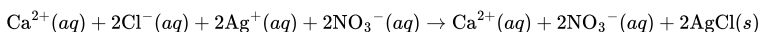


This balanced equation, derived in the usual fashion, is called a **molecular equation**, because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogeneously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

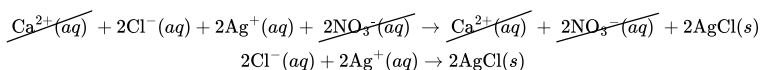


Unlike these three ionic compounds,  $\text{AgCl}$  does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

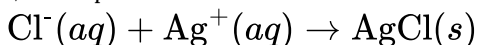
Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:



Examining this equation shows that two chemical species are present in identical form on both sides of the arrow,  $\text{Ca}^{2+}(aq)$  and  $\text{NO}_3^{-}(aq)$ . 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 succinct representation called a **net ionic equation**:



Following the convention of using the smallest possible integers as coefficients, this equation is then written:



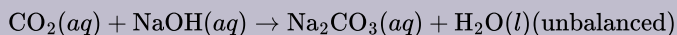
This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of  $\text{Cl}^{-}$  and  $\text{Ag}^{+}$ .

### Example 2: Molecular and Ionic Equations

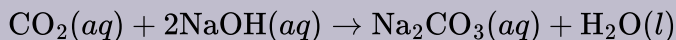
When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Show Answer

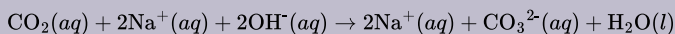
Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:



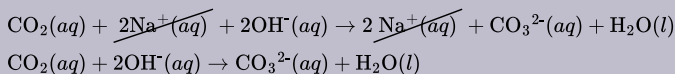
Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:



The two dissolved ionic compounds, NaOH and  $\text{Na}_2\text{CO}_3$ , can be represented as dissociated ions to yield the complete ionic equation:

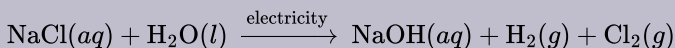


Finally, identify the spectator ion(s), in this case  $\text{Na}^+(aq)$ , and remove it from each side of the equation to generate the net ionic equation:



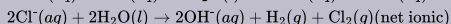
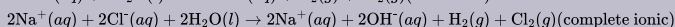
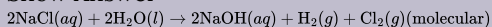
## Check Your Learning

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:



Write balanced molecular, complete ionic, and net ionic equations for this process.

### Show Answer



## Key Concepts and Summary

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. 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.

## *Exercises*

1. What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?
2. Consider molecular, complete ionic, and net ionic equations.
  - a. What is the difference between these types of equations?
  - b. In what circumstance would the complete and net ionic equations for a reaction be identical?
3. Write a balanced molecular equation describing each of the following chemical reactions.
  - a. Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.
  - b. Gaseous butane,  $\text{C}_4\text{H}_{10}$ , reacts with diatomic oxygen gas to yield gaseous carbon dioxide and

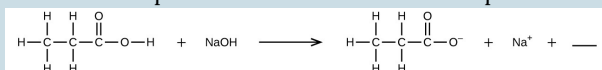


- water vapor.
- c. Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.
  - d. Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.
4. Write a balanced equation describing each of the following chemical reactions.
- a. Solid potassium chlorate,  $\text{KClO}_3$ , decomposes to form solid potassium chloride and diatomic oxygen gas.
  - b. Solid aluminum metal reacts with solid diatomic iodine to form solid  $\text{Al}_2\text{I}_6$ .
  - 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.
5. Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.
- 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  $\text{Fe}^+$  ions.)

6. Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



7. Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).
  - a. Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.
  - b. The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

8. A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.
- The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.
  - The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.
  - Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.
  - The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.
  - Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.
9. From the balanced molecular equations, write the complete ionic and net ionic equations for the following:
- $\text{K}_2\text{C}_2\text{O}_4(aq) + \text{Ba}(\text{OH})_2(aq) \rightarrow 2\text{KOH}(aq) + \text{BaC}_2\text{O}_4(s)$
  - $\text{Pb}(\text{NO}_3)_2(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(s) + 2\text{HNO}_3(aq)$
  - $\text{CaCO}_3(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CaSO}_4(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$

#### Show Selected Answers

- 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.

3. The balanced equations are as follows:

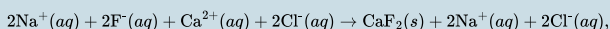
- a.  $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
- b.  $2\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 10\text{H}_2\text{O}(g)$
- c.  $\text{MgCl}_2(aq) + 2\text{NaOH}(aq) \rightarrow \text{Mg}(\text{OH})_2(s) + 2\text{NaCl}(aq)$
- d.  $2\text{H}_2\text{O}(g) + 2\text{Na}(s) \rightarrow 2\text{NaOH}(s) + \text{H}_2(g)$

5. The answers are as follows:

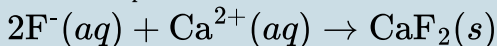
- a.  $\text{Ba}(\text{NO}_3)_2, \text{KClO}_3$
- b.  $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$
- c.  $2\text{Ba}(\text{NO}_3)_2(s) \rightarrow 2\text{BaO}(s) + 2\text{N}_2(g) + 5\text{O}_2(g)$   
 $2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s)$
- d.  $4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(g)$   
 $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$

7. The answers are as follows:

- a.  $4\text{HF}(aq) + \text{SiO}_2(s) \rightarrow \text{SiF}_4(g) + 2\text{H}_2\text{O}(l);$
- b. complete ionic equation:



net ionic equation:



9. The ionic and net ionic equations for each are as follows:

- a.  $2\text{K}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) + \text{Ba}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow 2\text{K}^+(aq) + 2\text{OH}^-(aq) + \text{BaC}_2\text{O}_4(s) \text{ (complete)}$   
 $\text{Ba}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \rightarrow \text{BaC}_2\text{O}_4(s) \text{ (net)}$
- b.  $\text{Pb}^{2+}(aq) + 2\text{NO}_3^-(aq) + 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) + 2\text{H}^+(aq) + 2\text{NO}_3^-(aq) \text{ (complete)}$   
 $\text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) \text{ (net)}$
- c.  $\text{CaCO}_3(s) + 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{CaSO}_4(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \text{ (complete)}$   
 $\text{CaCO}_3(s) + 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{CaSO}_4(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \text{ (net)}$

## Glossary

**balanced equation:** chemical equation with equal numbers of atoms for each element in the reactant and product

**chemical equation:** symbolic representation of a chemical reaction

**coefficient:** number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

**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

**molecular equation:** chemical equation in which all reactants and products are represented as neutral substances

**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)

**product:** substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

**reactant:** substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

**spectator ion:** ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

# 35. Classifying Chemical Reactions

## *Learning Objectives*

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

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

## Precipitation Reactions and Solubility Rules

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 (see the last module of this 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**. 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. More information on these important concepts is provided in the text chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds.

## Solubilities of Common Ionic Compounds in Water

**Soluble compounds** contain

- group 1 metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ ) and ammonium ion  $\text{NH}_4^+$
- the halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ )
- the acetate ( $\text{C}_2\text{H}_3\text{O}_2^-$ ), bicarbonate ( $\text{HCO}_3^-$ ), nitrate ( $\text{NO}_3^-$ ), and chlorate ( $\text{ClO}_3^-$ ) ions
- the sulfate ( $\text{SO}_4^{2-}$ ) ion

**Exceptions** to these solubility rules include

- halides of  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ , and  $\text{Pb}_2^+$
- sulfates of  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}_2^+$ , and  $\text{Sr}^{2+}$

**Insoluble compounds** contain

- carbonate ( $\text{CO}_3^{2-}$ ), chromate ( $\text{CrO}_4^{2-}$ ), phosphate ( $\text{PO}_4^{3-}$ ) and sulfide ( $\text{S}^{2-}$ ) ions
- hydroxide ion ( $\text{OH}^-$ )

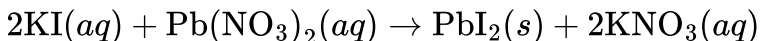
**Exceptions** to these insolubility rules include

- compounds of these anions with group 1 metal cations and ammonium ion
- hydroxides of group 1 metal cations and  $\text{Ba}^{2+}$

A vivid example of precipitation is observed when solutions of

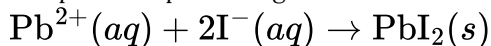


potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:



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.

The net ionic equation representing this reaction is:



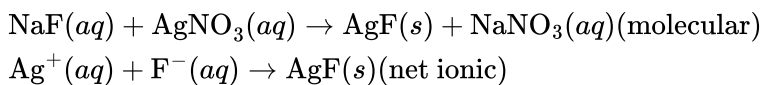
Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 1). The properties of pure  $\text{PbI}_2$  crystals make them useful for fabrication of X-ray and gamma ray detectors.

The solubility guidelines discussed above 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 solutions of silver nitrate and sodium fluoride will yield a solution containing  $\text{Ag}^+$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ , and  $\text{F}^-$  ions. Aside from the two ionic compounds originally present in the solutions,  $\text{AgNO}_3$  and  $\text{NaF}$ , two additional ionic compounds may be derived from this collection of ions:  $\text{NaNO}_3$  and  $\text{AgF}$ . The solubility guidelines indicate all nitrate salts are soluble but that  $\text{AgF}$  is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:



Figure 1. A precipitate of  $\text{PbI}_2$  forms when solutions containing  $\text{Pb}^{2+}$  and  $\text{I}^-$  are mixed. (credit: Der Kreole/Wikimedia Commons)



### *Example 1: Predicting Precipitation Reactions*

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.

1. potassium sulfate and barium nitrate
2. lithium chloride and silver acetate
3. lead nitrate and ammonium carbonate

Show Answer

1. The two possible products for this combination are  $\text{KNO}_3$  and  $\text{BaSO}_4$ , both of which are soluble per the tabulated guidelines. No precipitation is expected for  $\text{KNO}_3$ ;  $\text{BaSO}_4$  is a precipitate.
2. The two possible products for this combination are  $\text{LiC}_2\text{H}_3\text{O}_2$  and  $\text{AgCl}$ . The solubility guidelines indicate  $\text{AgCl}$  is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is  

$$\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s).$$
3. The two possible products for this combination are  $\text{PbCO}_3$  and  $\text{NH}_4\text{NO}_3$ , both of which are soluble per the tabulated guidelines. No precipitation is expected.

### *Check Your Learning*

Which solution could be used to precipitate the barium ion,  $\text{Ba}^{2+}$ , in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

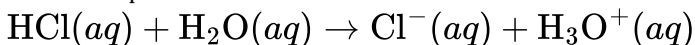
Show Answer

sodium sulfate,  $\text{BaSO}_4$

## Acid-Base Reactions

An **acid-base reaction** is one in which a hydrogen ion,  $\text{H}^+$ , is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions,  $\text{H}_3\text{O}^+$ . As an example, consider the equation shown here:



The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water,  $\text{H}_3\text{O}^+$  ions are

produced by a chemical reaction in which  $\text{H}^+$  ions are transferred from  $\text{HCl}$  molecules to  $\text{H}_2\text{O}$  molecules (Figure 2).

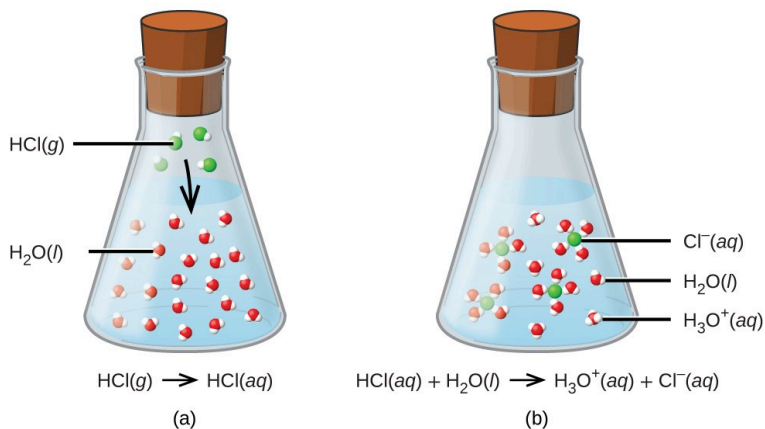
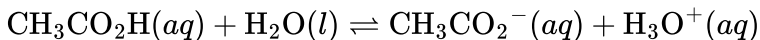


Figure 2. When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong (Table 1).

A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small

amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:



When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form,  $\text{CH}_3\text{CO}_2^-$  (Figure 3). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)

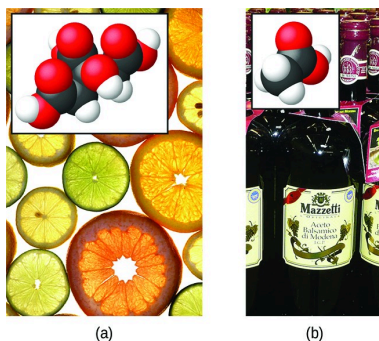


Figure 3. (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. The hydrogen atoms that may be transferred during an acid-base reaction are highlighted in the inset molecular structures. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

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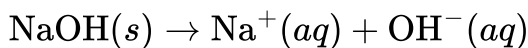
**Table 1. Common Strong Acids**

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO <sub>3</sub>	nitric acid
HClO <sub>4</sub>	perchloric acid
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid

---

A **base** is a substance that will dissolve in water to yield hydroxide ions, OH<sup>−</sup>. 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)<sub>2</sub>. When these compounds dissolve in water, hydroxide ions are released directly into the solution. For example, KOH and Ba(OH)<sub>2</sub> dissolve in water and dissociate completely to produce cations (K<sup>+</sup> and Ba<sup>2+</sup>, respectively) and hydroxide ions, OH<sup>−</sup>. These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

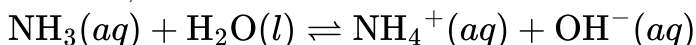
Consider as an example the dissolution of lye (sodium hydroxide) in water:



This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na<sup>+</sup> and OH<sup>−</sup> ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically

well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (Figure 4). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:



This is, by definition, an acid-base reaction, in this case involving the transfer of  $\text{H}^+$  ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as  $\text{NH}_4^+$  ions.



(a)

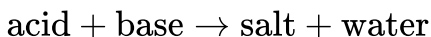


(b)

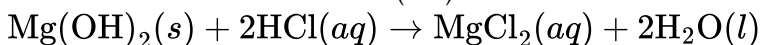
Figure 4. Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

The chemical reactions described in which acids and bases dissolved in water produce hydronium and hydroxide ions,

respectively, are, by definition, acid-base reactions. In these reactions, water serves as both a solvent *and* a reactant. A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often a **salt** and water, and neither reactant is the water itself:



To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid  $\text{Mg}(\text{OH})_2$ ) is ingested to ease symptoms associated with excess stomach acid ( $\text{HCl}$ ):



Note that in addition to water, this reaction produces a salt, magnesium chloride.

### *Example 2: Writing Equations for Acid-Base Reactions*

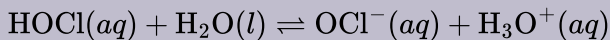
Write balanced chemical equations for the acid-base reactions described here:

1. the weak acid hydrogen hypochlorite reacts with water
2. a solution of barium hydroxide is neutralized with a solution of nitric acid

Show Answer

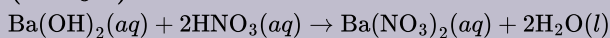
1. The two reactants are provided,  $\text{HOCl}$  and  $\text{H}_2\text{O}$ . Since the substance is reported to be an acid, its reaction with water will involve the transfer of  $\text{H}^+$  from  $\text{HOCl}$  to  $\text{H}_2\text{O}$  to generate hydronium ions,  $\text{H}_3\text{O}^+$  and hypochlorite ions,  $\text{OCl}^-$ :





. A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

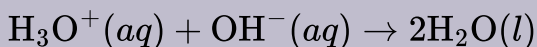
2. The two reactants are provided,  $\text{Ba}(\text{OH})_2$  and  $\text{HNO}_3$ . Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide ( $\text{Ba}^{2+}$ ) and the anion generated when the acid transfers its hydrogen ion ( $\text{NO}_3^-$ ):



### *Check Your Learning*

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Show Answer

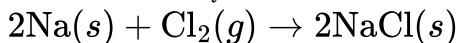


Explore the microscopic view of strong and weak acids and bases at the [PhET Acid-Base Simulator](#).

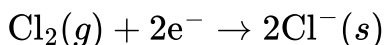
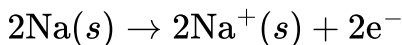
## Oxidation-Reduction Reactions

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:



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**:



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:

oxidation = loss of electrons

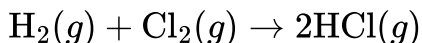
reduction = gain of electrons

In this reaction, then, sodium is *oxidized* and chlorine is *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.

reducing agent = species that is oxidized

oxidizing agent = 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:



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 was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

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,  $\text{O}_2^{2-}$ ), very rarely  $-\frac{1}{2}$  (so-called superoxides,  $\text{O}_2^-$ ), 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 3: Assigning Oxidation Numbers*

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

1.  $\text{H}_2\text{S}$
2.  $\text{SO}_3^{2-}$
3.  $\text{Na}_2\text{SO}_4$

Show Answer

1. According to guideline 1, 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:  
$$\text{charge on H}_2\text{S} = 0 = (2 \times +1) + (1 \times x)$$
$$x = 0 - (2 \times +1) = -2$$
2. 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:  
$$\text{charge on SO}_3^{2-} = -2 = (3 \times -1) + (1 \times x)$$
$$x = -2 - (3 \times -2) = +4$$

3. 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:
- $$\text{charge on SO}_4^{2-} = -2 = (4 \times -2) + (1 \times x)$$
- $$x = -2 - (4 \times -2) = +6$$

### *Check Your Learning*

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

1.  $\text{K}\underline{\text{N}}\text{O}_3$
2.  $\underline{\text{Al}}\text{H}_3$
3.  $\underline{\text{N}}\text{H}_4^+$
4.  $\text{H}_2\underline{\text{P}}\text{O}_4^-$

Show Answer

1. N, +5
2. Al, +3
3. N, -3
4. P, +5

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

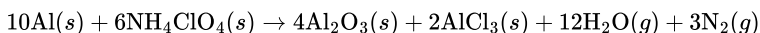
of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist, as in Example 4.) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

**oxidation = increase in oxidation number**

**reduction = decrease in oxidation number**

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<sub>2</sub> to -1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H<sub>2</sub> to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl<sub>2</sub> 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:



Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System 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.

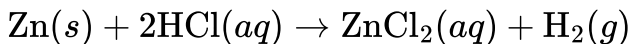


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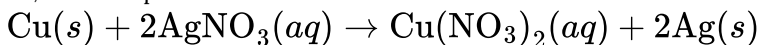
can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=58#oembed-1>

**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:



Metallic elements may also be oxidized by solutions of other metal salts; for example:



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  $\text{Cu}^{2+}$  ions dissolve in the solution to yield a characteristic blue color (Figure 5).

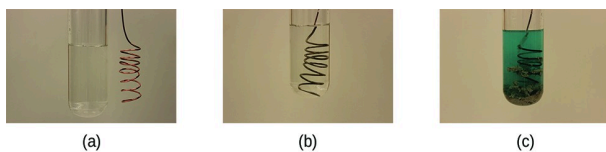
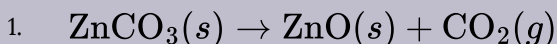


Figure 5. (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

### Example 4: 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.





2.  $2\text{Ga}(l) + 3\text{Br}_2(l) \rightarrow 2\text{GaBr}_3(s)$
3.  $2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
4.  $\text{BaCl}_2(aq) + \text{K}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + 2\text{KCl}(aq)$
5.  $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

Show Answer

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

1. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
2. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in  $\text{Ga}(l)$  to +3 in  $\text{GaBr}_3(s)$ . The reducing agent is  $\text{Ga}(l)$ . Bromine is reduced, its oxidation number decreasing from 0 in  $\text{Br}_2(l)$  to -1 in  $\text{GaBr}_3(s)$ . The oxidizing agent is  $\text{Br}_2(l)$ .
3. 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  $\text{H}_2\text{O}_2(aq)$  to 0 in  $\text{O}_2(g)$ . Oxygen is also reduced, its oxidation number decreasing from -1 in  $\text{H}_2\text{O}_2(aq)$  to -2 in  $\text{H}_2\text{O}(l)$ . For disproportionation reactions, the same substance functions as an oxidant and a reductant.
4. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
5. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from -2 in  $\text{C}_2\text{H}_4(g)$  to +4 in  $\text{CO}_2(g)$ . The reducing agent (fuel) is  $\text{C}_2\text{H}_4(g)$ . Oxygen is reduced, its oxidation number

decreasing from 0 in  $\text{O}_2(g)$  to  $-2$  in  $\text{H}_2\text{O}(l)$ . The oxidizing agent is  $\text{O}_2(g)$ .

### *Check Your Learning*

This equation describes the production of tin(II) chloride:  
$$\text{Sn}(s) + 2\text{HCl}(g) \rightarrow \text{SnCl}_2(s) + \text{H}_2(g)$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Show Answer

Yes, a single-replacement reaction.  $\text{Sn}(s)$  is the reductant,  $\text{HCl}(g)$  is the oxidant.

## Balancing Redox Reactions via the Half-Reaction Method

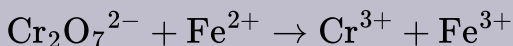
Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations 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:

1. Write the two half-reactions representing the redox process.

2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding  $\text{H}_2\text{O}$  molecules.
4. Balance hydrogen atoms by adding  $\text{H}^+$  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:
  - Add  $\text{OH}^-$  ions to both sides of the equation in numbers equal to the number of  $\text{H}^+$  ions.
  - On the side of the equation containing both  $\text{H}^+$  and  $\text{OH}^-$  ions, combine these ions to yield water molecules.
  - Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges<sup>2</sup> are balanced.

### *Example 5: Balancing Redox Reactions in Acidic Solution*

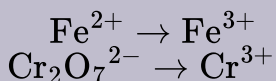
Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.



Show Answer

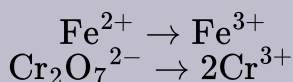
*Step 1. Write the two half-reactions.*

Each half-reaction will contain one reactant and one product with one element in common.



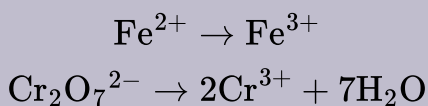
*Step 2. Balance all elements except oxygen and hydrogen.*

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.



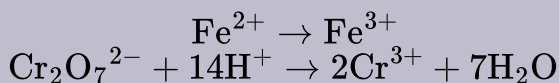
*Step 3. Balance oxygen atoms by adding H<sub>2</sub>O molecules.*

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.



*Step 4. Balance hydrogen atoms by adding H<sup>+</sup> ions.*

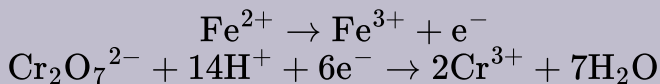
The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.



*Step 5. Balance charge by adding electrons.*

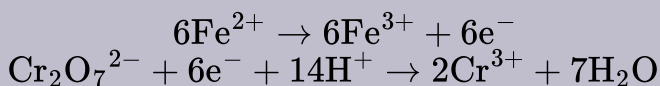
The iron half-reaction shows a total charge of 2+ on the left side (1 Fe<sup>2+</sup> ion) and 3+ on the right side (1 Fe<sup>3+</sup> ion). Adding one electron to the right side bring that side's total charge to (3+) + (1-) = 2+, and charge balance is achieved.

The chromium half-reaction shows a total charge of (1 × 2-) + (14 × 1+) = 12+ on the left side (1 Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion and 14 H<sup>+</sup> ions). The total charge on the right side is (2 × 3+) = 6 + (2 Cr<sup>3+</sup> ions). Adding six electrons to the left side will bring that side's total charge to (12+ + 6-) = 6+, and charge balance is achieved.

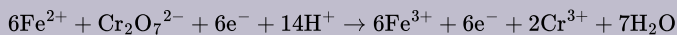


*Step 6. Multiply the two half-reactions.*

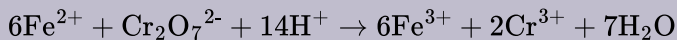
This step makes it so the number of electrons in one reaction equals the number of electrons in the other reaction. To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.



*Step 7. Add the balanced half-reactions and cancel species that appear on both sides of the equation.*



Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:



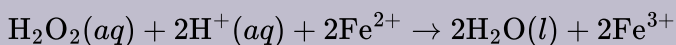
A final check of atom and charge balance confirms the equation is balanced.

	Reactants	Products
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

### *Check Your Learning*

In acidic solution, hydrogen peroxide reacts with  $\text{Fe}^{2+}$  to produce  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}$ . Write a balanced equation for this reaction.

Show Answer



### *Key Concepts and Summary*

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and oxidation-reduction (redox). Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants. Redox reactions involve a change in oxidation number for one or more reactant elements.

Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

## Exercises

1. Use the following equations to answer the next four questions:

- $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$
  - $\text{Na}^+(aq) + \text{Cl}^-(aq) \text{Ag}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{AgCl}(s) + \text{Na}^+(aq) + \text{NO}_3^-(aq)$
  - $\text{CH}_3\text{OH}(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g)$
  - $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$
  - $\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$
- a. Which equation describes a physical change?
  - b. Which equation identifies the reactants and products of a combustion reaction?
  - c. Which equation is not balanced?
  - d. Which is a net ionic equation?

2. Indicate what type, or types, of reaction each of the following represents:

- a.  $\text{Ca}(s) + \text{Br}_2(l) \rightarrow \text{CaBr}_2(s)$
- b.  $\text{Ca}(\text{OH})_2(aq) + 2\text{HBr}(aq) \rightarrow \text{CaBr}_2(aq) + 2\text{H}_2\text{O}(l)$
- c.  $\text{C}_6\text{H}_{12}(l) + 9\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$

3. Indicate what type, or types, of reaction each of the following represents:



- a.  $\text{H}_2\text{O}(g) + \text{C}(s) \rightarrow \text{CO}(g) + \text{H}_2(g)$
- b.  $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$
- c.  $\text{Al}(\text{OH})_3(aq) + 3\text{HCl}(aq) \rightarrow \text{AlBr}_3(aq) + 3\text{H}_2\text{O}(l)$
- d.  $\text{Pb}(\text{NO}_3)_2(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(s) + 2\text{HNO}_3(aq)$
4. Silver can be separated from gold because silver dissolves in nitric acid while gold does not. Is the dissolution of silver in nitric acid an acid-base reaction or an oxidation-reduction reaction? Explain your answer.
5. Determine the oxidation states of the elements in the following compounds:
- a. NaI
- b.  $\text{GdCl}_3$
- c.  $\text{LiNO}_3$
- d.  $\text{H}_2\text{Se}$
- e.  $\text{Mg}_2\text{Si}$
- f.  $\text{RbO}_2$ , rubidium superoxide
- g. HF
6. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.
- a.  $\text{H}_3\text{PO}_4$
- b.  $\text{Al}(\text{OH})_3$
- c.  $\text{SeO}_2$
- d.  $\text{KNO}_2$
- e.  $\text{In}_2\text{S}_3$
- f.  $\text{P}_4\text{O}_6$
7. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing

compounds are peroxides or superoxides.

- a.  $\text{H}_2\text{SO}_4$
- b.  $\text{Ca}(\text{OH})_2$
- c.  $\text{BrOH}$
- d.  $\text{ClNO}_2$
- e.  $\text{TiCl}_4$
- f.  $\text{NaH}$

8. Classify the following as acid-base reactions or oxidation-reduction reactions:

- a.  $\text{Na}_2\text{S}(aq) + 2\text{HCl}(aq) \rightarrow 2\text{NaCl}(aq) + \text{H}_2\text{S}(g)$
- b.  $2\text{Na}(s) + 2\text{HCl}(aq) \rightarrow 2\text{NaCl}(aq) + \text{H}_2(g)$
- c.  $\text{Mg}(s) + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s)$
- d.  $\text{MgO}(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l)$
- e.  $\text{K}_3\text{P}(s) + 2\text{O}_2(g) \rightarrow \text{K}_3\text{PO}_4(s)$
- f.  $3\text{KOH}(aq) + \text{H}_3\text{PO}_4(aq) \rightarrow \text{K}_3\text{PO}_4(aq) + 3\text{H}_2\text{O}(l)$

9. 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:

- a.  $\text{Mg}(s) + \text{NiCl}_2(aq) \rightarrow \text{MgCl}_2(aq) + \text{Ni}(s)$
- b.  $\text{PCl}_3(l) + \text{Cl}_2(g) \rightarrow \text{PCl}_5(s)$
- c.  $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
- d.  $\text{Zn}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{H}_2(g)$
- e.  $2\text{K}_2\text{S}_2\text{O}_3(s) + \text{I}_2(s) \rightarrow \text{K}_2\text{S}_4\text{O}_6(s) + 2\text{KI}(s)$
- f.  $3\text{Cu}(s) + 8\text{HNO}_3(aq) \rightarrow 3\text{Cu}(\text{NO}_3)_2(aq) + 2\text{NO}(g) + 4\text{H}_2\text{O}(l)$

10. Complete and balance the following acid-base equations:

- a.  $\text{HCl}$  gas reacts with solid  $\text{Ca}(\text{OH})_2(s)$ .

- b. A solution of  $\text{Sr}(\text{OH})_2$  is added to a solution of  $\text{HNO}_3$ .
11. Complete and balance the following acid-base equations:
- a. A solution of  $\text{HClO}_4$  is added to a solution of  $\text{LiOH}$ .
- b. Aqueous  $\text{H}_2\text{SO}_4$  reacts with  $\text{NaOH}$ .
- c.  $\text{Ba}(\text{OH})_2$  reacts with  $\text{HF}$  gas.
12. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.
- a.  $\text{Al}(s) + \text{F}_2(g) \rightarrow$
- b.  $\text{Al}(s) + \text{CuBr}_2(aq) \rightarrow$  (single displacement)
- c.  $\text{P}_4(s) + \text{O}_2(g) \rightarrow$
- d.  $\text{Ca}(s) + \text{H}_2\text{O}(l) \rightarrow$  (products are a strong base and a diatomic gas)
13. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.
- a.  $\text{K}(s) + \text{H}_2\text{O}(l) \rightarrow$
- b.  $\text{Ba}(s) + \text{HBr}(aq) \rightarrow$
- c.  $\text{Sn}(s) + \text{I}_2(s) \rightarrow$
14. Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more

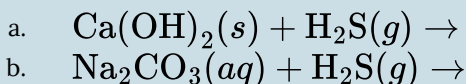
than one correct answer, depending on the amounts of reactants used.

- a.  $\text{Mg}(\text{OH})_2(s) + \text{HClO}_4(aq) \rightarrow$
- b.  $\text{SO}_3(g) + \text{H}_2\text{O}(l) \rightarrow$  (assume an excess of water and that the product dissolves)
- c.  $\text{SrO}(s) + \text{H}_2\text{SO}_4(l) \rightarrow$

- 15. When heated to 700–800 °C, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.
- 16. The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?
- 17. Write the molecular, total ionic, and net ionic equations for the following reactions:
  - a.  $\text{Ca}(\text{OH})_2(aq) + \text{HC}_2\text{H}_3\text{O}_2(aq) \rightarrow$
  - b.  $\text{H}_3\text{PO}_4(aq) + \text{CaCl}_2(aq) \rightarrow$
- 18. Great Lakes Chemical Company produces bromine,  $\text{Br}_2$ , from bromide salts such as  $\text{NaBr}$ , in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of  $\text{NaBr}$  with  $\text{Cl}_2$ .
- 19. In a common experiment in the general chemistry laboratory, magnesium metal is heated in air to produce  $\text{MgO}$ .  $\text{MgO}$  is a white solid, but in these experiments it often looks gray, due to small amounts of  $\text{Mg}_3\text{N}_2$ , a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.
- 20. Lithium hydroxide may be used to absorb carbon

dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO<sub>2</sub>. (Hint: Water is one of the products.)

21. Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, CaCO<sub>3</sub>, with propionic acid, C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>H, which has properties similar to those of acetic acid. Write the balanced equation for the formation of calcium propionate.
22. Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:



23. Copper(II) sulfide is oxidized by molecular oxygen to produce gaseous sulfur trioxide and solid copper(II) oxide. The gaseous product then reacts with liquid water to produce liquid hydrogen sulfate as the only product. Write the two equations which represent these reactions.
24. Write balanced chemical equations for the reactions used to prepare each of the following compounds from the given starting material(s). In some cases, additional reactants may be required.
- a. solid ammonium nitrate from gaseous molecular nitrogen via a two-step process (first reduce the nitrogen to ammonia, then neutralize the ammonia with an appropriate acid)

- b. gaseous hydrogen bromide from liquid molecular bromine via a one-step redox reaction
  - c. gaseous  $\text{H}_2\text{S}$  from solid Zn and S via a two-step process (first a redox reaction between the starting materials, then reaction of the product with a strong acid)
25. Calcium cyclamate  $\text{Ca}(\text{C}_6\text{H}_{11}\text{NHSO}_3)_2$  is an artificial sweetener used in many countries around the world but is banned in the United States. It can be purified industrially by converting it to the barium salt through reaction of the acid  $\text{C}_6\text{H}_{11}\text{NHSO}_3\text{H}$  with barium carbonate, treatment with sulfuric acid (barium sulfate is very insoluble), and then neutralization with calcium hydroxide. Write the balanced equations for these reactions.
  26. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):
    - a.  $\text{Sn}^{4+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq})$
    - b.  $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq}) \rightarrow \text{Ag}(\text{s}) + \text{NH}_3(\text{aq})$
    - c.  $\text{Hg}_2\text{Cl}_2(\text{s}) \rightarrow \text{Hg}(\text{l}) + \text{Cl}^-(\text{aq})$
    - d.  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{in acidic solution})$
    - e.  $\text{IO}_3^-(\text{aq}) \rightarrow \text{I}_2(\text{s})$
    - f.  $\text{SO}_3^{2-}(\text{aq}) \rightarrow \text{SO}_4^{2-}(\text{aq})$  (in acidic solution)
    - g.  $\text{MnO}_4^-(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq})$  (in acidic solution)
    - h.  $\text{Cl}^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq})$  (in basic solution)
  27. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):
    - a.  $\text{Cr}^{2+}(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq})$

- b.  $\text{Hg}(l) + \text{Br}^-(aq) \rightarrow \text{HgBr}_4^{2-}(aq)$
- c.  $\text{ZnS}(s) \rightarrow \text{Zn}(s) + \text{S}^{2-}(aq)$
- d.  $\text{H}_2(g) \rightarrow \text{H}_2\text{O}(l)$  (in basic solution)
- e.  $\text{H}_2(g) \rightarrow \text{H}_3\text{O}^+(aq)$  (in acidic solution)
- f.  $\text{NO}_3^-(aq) \rightarrow \text{HNO}_2(aq)$  (in acidic solution)
- g.  $\text{MnO}_2(s) \rightarrow \text{MnO}_4^-(aq)$  (in basic solution)
- h.  $\text{Cl}^-(aq) \rightarrow \text{ClO}_3^-(aq)$  (in acidic solution)

28. Balance each of the following equations according to the half-reaction method:

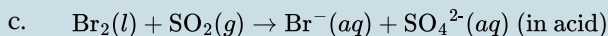
- a.  $\text{Sn}^{2+}(aq) + \text{Cu}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + \text{Cu}^+(aq)$
- b.  $\text{H}_2\text{S}(g) + \text{Hg}_2^{2+}(aq) \rightarrow \text{Hg}(l) + \text{S}(s)$  (in acid)
- c.  $\text{CN}^-(aq) + \text{ClO}_2(aq) \rightarrow \text{CNO}^-(aq) + \text{Cl}^-(aq)$  (in acid)
- d.  $\text{Fe}^{2+}(aq) + \text{Ce}^{4+}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Ce}^{3+}(aq)$
- e.  $\text{HBrO}(aq) \rightarrow \text{Br}^-(aq) + \text{O}_2(g)$  (in acid)

29. Balance each of the following equations according to the half-reaction method:

- a.  $\text{Zn}(s) + \text{NO}_3^-(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{N}_2(g)$  (in acid)
- b.  $\text{Zn}(s) + \text{NO}_3^-(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{NH}_3(aq)$  (in base)
- c.  $\text{CuS}(s) + \text{NO}_3^-(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{S}(s) + \text{NO}(g)$  (in acid)
- d.  $\text{NH}_3(aq) + \text{O}_2(g) \rightarrow \text{NO}_2(g)$  (gas phase)
- e.  $\text{Cl}_2(g) + \text{OH}^-(aq) \rightarrow \text{Cl}^-(aq) + \text{ClO}_3^-(aq)$  (in base)
- f.  $\text{H}_2\text{O}_2(aq) + \text{MnO}_4^-(aq) \rightarrow \text{Mn}^{2+}(aq) + \text{O}_2(g)$  (in acid)
- g.  $\text{NO}_2(g) \rightarrow \text{NO}_3^-(aq) + \text{NO}_2^-(aq)$  (in base)
- h.  $\text{Fe}^{3+}(aq) + \text{I}^-(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{I}_2(aq)$

30. Balance each of the following equations according to the half-reaction method:

- a.  $\text{MnO}_4^-(aq) + \text{NO}_2^-(aq) \rightarrow \text{MnO}_2(s) + \text{NO}_3^-(aq)$  (in base)
- b.  $\text{MnO}_4^{2-}(aq) \rightarrow \text{MnO}_4^-(aq) + \text{MnO}_2(s)$  (in base)



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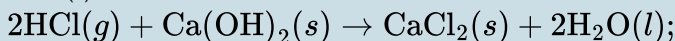
2. (a) oxidation-reduction (addition); (b) acid-base (neutralization); (c) oxidation-reduction (combustion)

4. An oxidation-reduction reaction, because the oxidation state of the silver changes during the reaction.

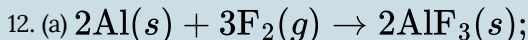
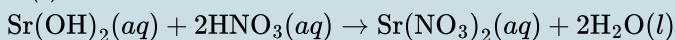
6. (a) H +1, P +5, O -2; (b) Al +3, H +1, O -2; (c) Se +4, O -2; (d) K +1, N +3, O -2; (e) In +3, S -2; (f) P +3, O -2

8. (a) acid-base; (b) oxidation-reduction: Na is oxidized,  $\text{H}^+$  is reduced; (c) oxidation-reduction: Mg is oxidized,  $\text{Cl}_2$  is reduced; (d) acid-base; (e) oxidation-reduction:  $\text{P}^{3-}$  is oxidized,  $\text{O}_2$  is reduced; (f) acid-base

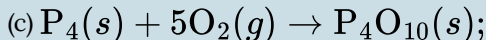
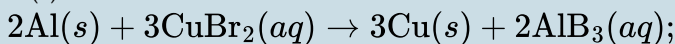
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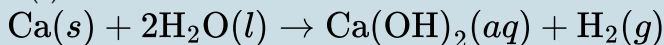
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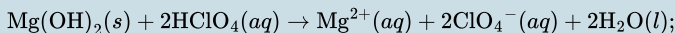
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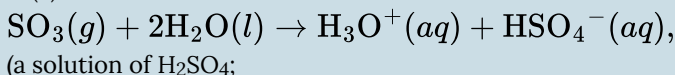
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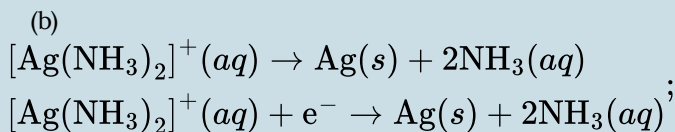
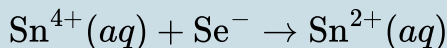
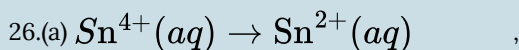
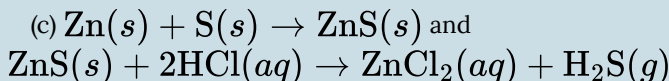
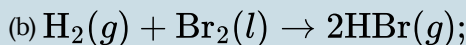
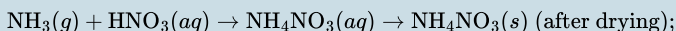
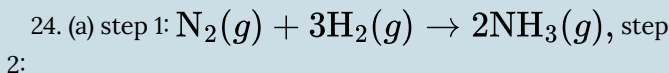
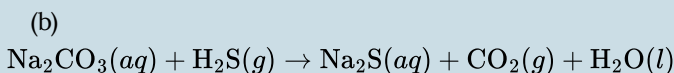
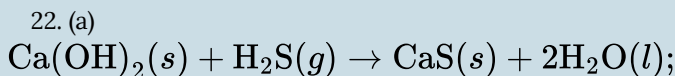
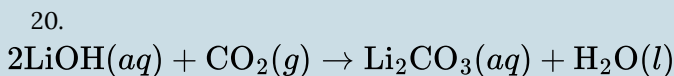
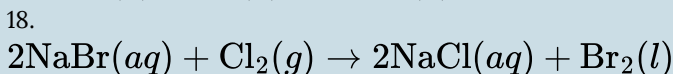
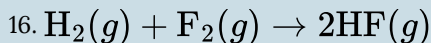
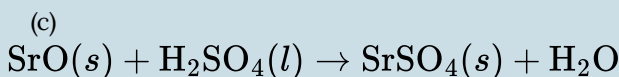
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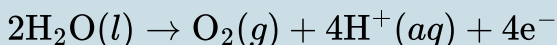
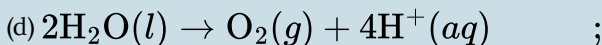
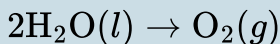
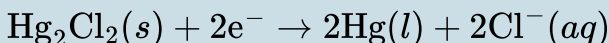
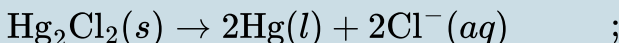
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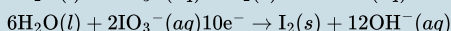
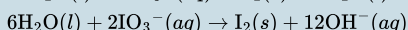
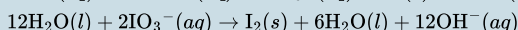
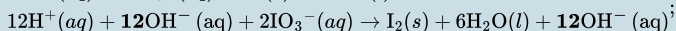
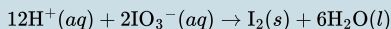
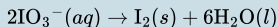
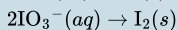
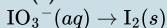




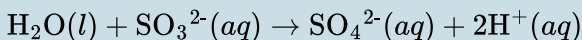
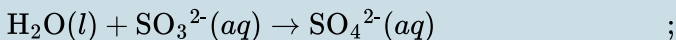
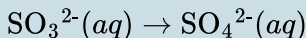
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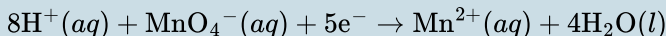
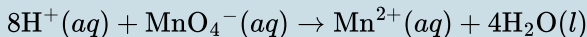
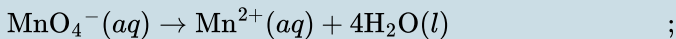
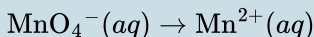
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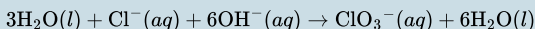
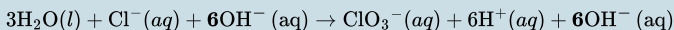
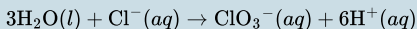
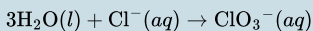
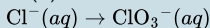
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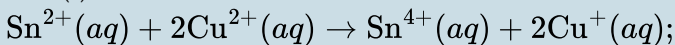
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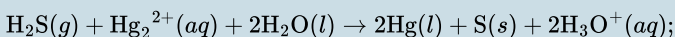
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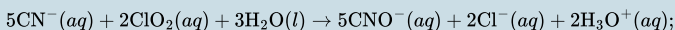
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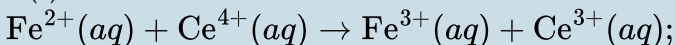
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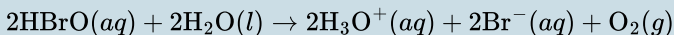
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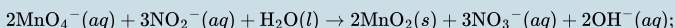
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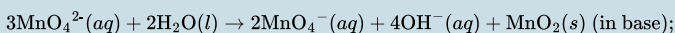
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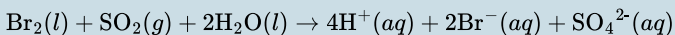
30. (a)



(b)



(c)



## Glossary

**acid:** substance that produces  $\text{H}_3\text{O}^{+}$  when dissolved in water

**acid-base reaction:** reaction involving the transfer of a hydrogen ion between reactant species

**base:** substance that produces  $\text{OH}^-$  when dissolved in water

**combustion reaction:** vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

**half-reaction:** an equation that shows whether each reactant loses or gains electrons in a reaction.

**insoluble:** of relatively low solubility; dissolving only to a slight extent

**neutralization reaction:** reaction between an acid and a base to produce salt and water

**oxidation:** process in which an element's oxidation number is increased by loss of electrons

**oxidation-reduction reaction:** (also, redox reaction) reaction involving a change in oxidation number for one or more reactant elements

**oxidation number:** (also, oxidation state) the charge each atom of an element would have in a compound if the compound were ionic

**oxidizing agent:** (also, oxidant) substance that brings about the oxidation of another substance, and in the process becomes reduced

**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

**reduction:** process in which an element's oxidation number is decreased by gain of electrons

**reducing agent:** (also, reductant) substance that brings about the reduction of another substance, and in the process becomes oxidized

**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

**single-displacement reaction:** (also, replacement) redox reaction

involving the oxidation of an elemental substance by an ionic species

**soluble:** of relatively high solubility; dissolving to a relatively large extent

**solubility:** the extent to which a substance may be dissolved in water, or any solvent

**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

**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



PART IX

# REACTION MATHEMATICS





# 36. Formula Mass and the Mole Concept

## *Learning Objectives*

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

- Calculate formula masses for covalent and ionic compounds
- Define the amount unit mole and the related quantity Avogadro's number
- Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these 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.

## Formula Mass

In an earlier chapter, we described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the **formula mass** of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

### Formula Mass for Covalent Substances

For covalent 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. Consider chloroform ( $\text{CHCl}_3$ ), 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 molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

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

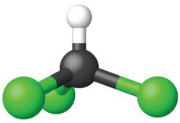


Figure 1. The average mass of a chloroform molecule,  $\text{CHCl}_3$ , is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Likewise, the molecular mass of an aspirin molecule,  $\text{C}_9\text{H}_8\text{O}_4$ , 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 2).

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
<b>Molecular mass</b>					<b>180.15</b>

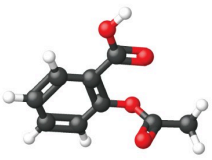


Figure 2. The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin,  $\text{C}_9\text{H}_8\text{O}_4$ .

### *Example 1: Computing Molecular Mass for a Covalent Compound*

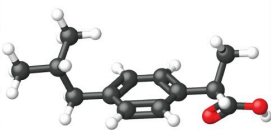
Ibuprofen,  $\text{C}_{13}\text{H}_{18}\text{O}_2$ , is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Show Answer

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	x	12.01	=	156.13
H	18	x	1.008	=	18.114
O	2	x	16.00	=	32.00
Molecular mass					206.27



### *Check Your Learning*

Acetaminophen,  $\text{C}_8\text{H}_9\text{NO}_2$ , 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?

Show Answer

151.16 amu

## Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the “molecular mass.”

As an example, consider sodium chloride,  $\text{NaCl}$ , the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations,  $\text{Na}^+$ , and chloride anions,  $\text{Cl}^-$ ,

combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (see Figure 3).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
Formula mass					58.44

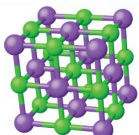


Figure 3. Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

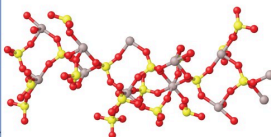
## Example 2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Show Answer

The formula for this compound indicates it contains  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  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,  $\text{Al}_2\text{S}_3\text{O}_{12}$ . 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	



## Check Your Learning

Calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Show Answer

310.18 amu

## The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water,  $\text{H}_2\text{O}$ , and hydrogen peroxide,  $\text{H}_2\text{O}_2$ , are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

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. A **mole** is defined as *the amount of substance containing the same number of discrete entities (atoms, molecules, ions, etc.) as the number of atoms in a sample of pure  $^{12}\text{C}$  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 an extremely important fundamental property, number of atoms, molecules, and so forth.

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. This constant is properly reported with an explicit unit of “per

mole,” a conveniently rounded version being  $6.022 \times 10^{23}/\text{mol}$ .

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 (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see Figure 4).

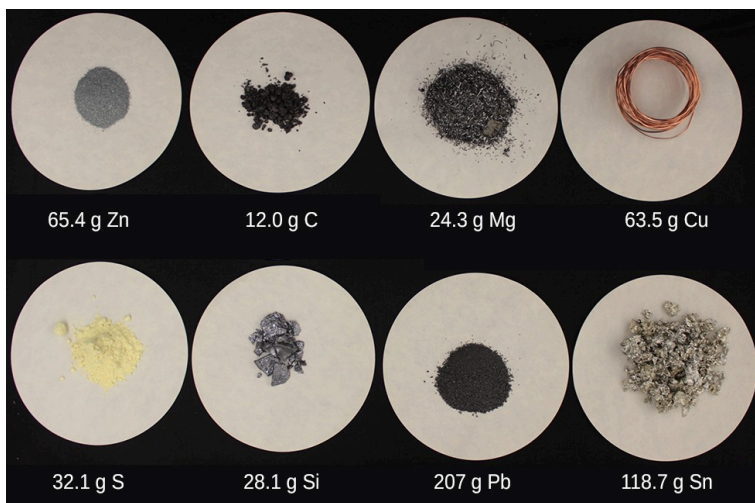


Figure 4. Each sample contains  $6.022 \times 10^{23}$  atoms—1.00 mol of atoms. From left to right (top row): 65.4g zinc, 12.0g carbon, 24.3g magnesium, and 63.5g copper. From left to right (bottom row): 32.1g sulfur, 28.1g silicon, 207g lead, and 118.7g tin. (credit: modification of work by Mark Ott)

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance,  $^{12}\text{C}$ , the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single  $^{12}\text{C}$  atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of  $^{12}\text{C}$  contains 1 mole of  $^{12}\text{C}$  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,  $^{12}\text{C}$ . Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure 5).



Figure 5. Each sample contains  $6.02 \times 10^{23}$  molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2g of  $\text{C}_8\text{H}_{17}\text{OH}$  (1-octanol, formula mass 130.2 amu), 454.9g of  $\text{HgI}_2$  (mercury(II) iodide, formula mass 459.9 amu), 32.0g of  $\text{CH}_3\text{OH}$  (methanol, formula mass 32.0 amu) and 256.5g of  $\text{S}_8$  (sulfur, formula mass 256.6 amu). (credit: Sahar Atwa)

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	$6.022 \times 10^{23}$
H	1.008	1.008	$6.022 \times 10^{23}$
O	16.00	16.00	$6.022 \times 10^{23}$
Na	22.99	22.99	$6.022 \times 10^{23}$
Cl	33.45	33.45	$6.022 \times 10^{23}$

While atomic mass and molar mass 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



Figure 6. A single drop of water.

water weighing about 0.03 g (see Figure 6). The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth.

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.

The mole is used in chemistry to represent  $6.022 \times 10^{23}$  of something, but it can be difficult to conceptualize such a large number. Watch this video to learn more.



*One or more interactive elements has been excluded from this version of the text. You can view them online here:*

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=60#oembed-1>

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate 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.

### *Example 3: Deriving Moles from Grams for an Element*

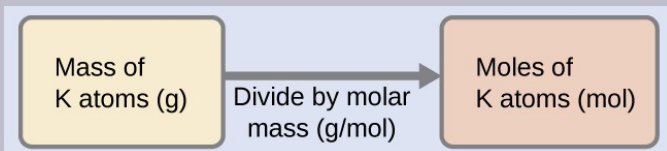
According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Show Answer

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.”

$$4.7 \cancel{\text{g}} \text{K} \left( \frac{\text{mol K}}{39.10 \cancel{\text{g}}} \right) = 0.12 \text{mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

### *Check Your Learning*

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?

Show Answer

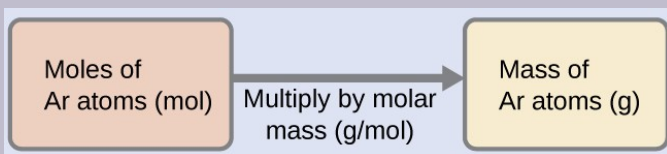
0.360 mol

### Example 4: Deriving Grams from Moles for an Element

A liter of air contains  $9.2 \times 10^{-4}$  mol argon. What is the mass of Ar in a liter of air?

Show Answer

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 ( $\sim 0.04$  g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4} \cancel{\text{mol Ar}} \left( \frac{39.95\text{g}}{\cancel{\text{mol Ar}}} \right) = 0.037\text{g Ar}$$

The result is in agreement with our expectations as noted above, around 0.04 g Ar.

### *Check Your Learning*

What is the mass of 2.561 mol of gold?

Show Answer

504.4 g

### *Example 5: Deriving Number of Atoms from Mass for an Element*

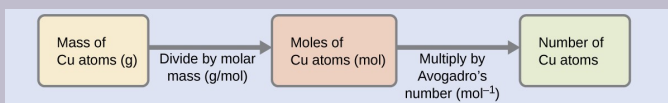
Copper is commonly used to fabricate electrical wire (Figure 7). How many copper atoms are in 5.00 g of copper wire?



*Figure 7. Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)*

#### Show Answer

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 ( $N_A$ ) 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:

$$5.00 \cancel{\text{g}}_{\text{Cu}} \left( \frac{\cancel{\text{mol Cu}}}{63.55 \cancel{\text{g}}} \right) \left( \frac{6.022 \times 10^{23} \text{atoms}}{\cancel{\text{mol}}} \right) = 4.74 \times 10^{22} \text{atoms of copper}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of  $10^{22}$  as expected.

### *Check Your Learning*

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?

Show Answer

$$4.586 \times 10^{22} \text{Au atoms}$$

### *Example 6: Deriving Moles from Grams for a*

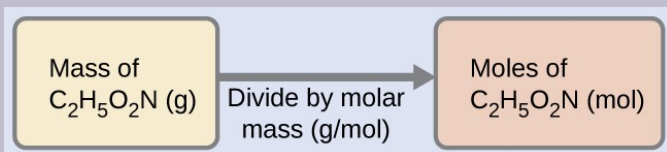


## Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula  $\text{C}_2\text{H}_5\text{O}_2\text{N}$ . How many moles of glycine molecules are contained in 28.35 g of glycine?

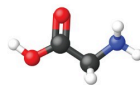
Show Answer

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 3:



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,  $\text{C}_2\text{H}_5\text{O}_2\text{N}$ , 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:

$$28.35 \cancel{\text{g}} \text{ glycine} \left( \frac{\text{mol glycine}}{75.07 \cancel{\text{g}}} \right) = 0.378 \text{ mol glycine}$$

This result is consistent with our rough estimate.

### Check Your Learning

How many moles of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , are in a 25-g sample of sucrose?

Show Answer

0.073 mol

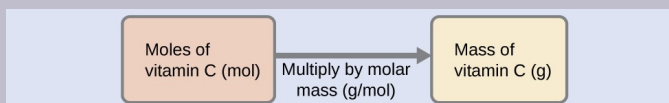
### Example 7: Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula  $\text{C}_6\text{H}_8\text{O}_6$ . The recommended daily dietary allowance of vitamin C for children aged 4–8 years is

$1.42 \times 10^{-4} \text{ mol}$ . What is the mass of this allowance in grams?

Show Answer

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 ( $\sim 10^{-4}$  or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass ( $\sim 0.02$  g). Performing the calculation, we get:

$$1.42 \times 10^{-4} \cancel{\text{mol vitamin C}} \left( \frac{176.124 \text{ g}}{\cancel{\text{mol vitamin C}}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

### *Check Your Learning*

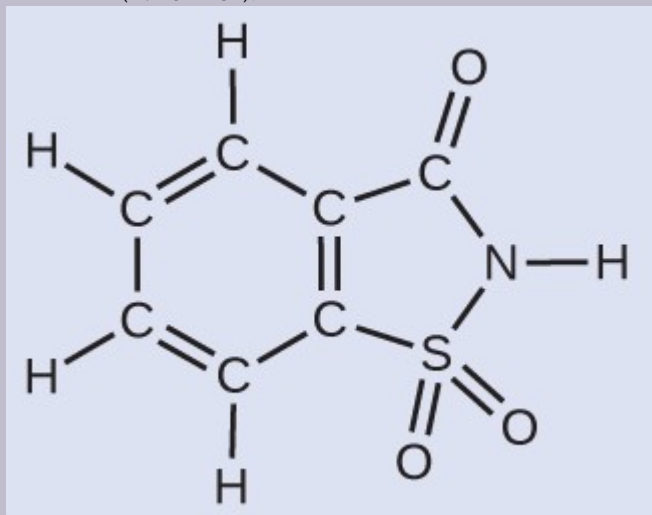
What is the mass of 0.443 mol of hydrazine,  $\text{N}_2\text{H}_4$ ?

Show Answer

14.2 g

### *Example 8: Deriving the Number of Atoms and Molecules from the Mass of a Compound*

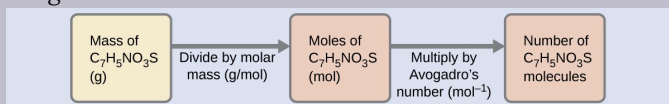
A packet of an artificial sweetener contains 40.0 mg of saccharin ( $\text{C}_7\text{H}_5\text{NO}_3\text{S}$ ), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Show Answer

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in Figure 5, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400 \text{ g C}_7\text{H}_5\text{NO}_3\text{S} \left( \frac{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}}{183.18 \text{ g C}_7\text{H}_5\text{NO}_3\text{S}} \right) \left( \frac{6.022 \times 10^{23} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}}{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}} \right) = 1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules} \left( \frac{7 \text{ C atoms}}{1 \text{ C}_7\text{H}_5\text{NO}_3\text{S molecule}} \right) = 9.20 \times 10^{21} \text{ C atoms}$$

### Check Your Learning

How many C<sub>4</sub>H<sub>10</sub> molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Show Answer

$9.545 \times 10^{22}$  molecules C<sub>4</sub>H<sub>10</sub>;  $9.545 \times 10^{23}$  atoms H

## Counting Neurotransmitter Molecules in the Brain

The brain is the control center of the central nervous system (Figure 8). 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 (more details available at the [White House's website](#)).

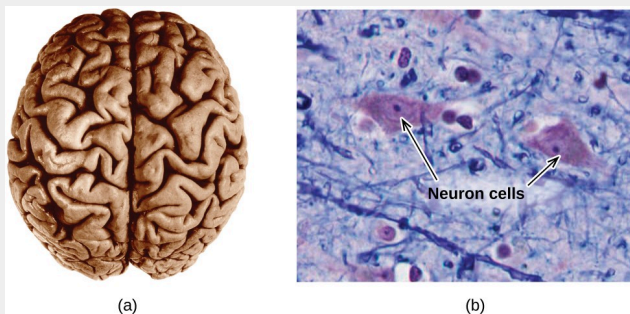


Figure 8. (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600 $\times$  magnification).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling 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 9). One neurotransmitter that has been very extensively studied is dopamine,  $\text{C}_8\text{H}_{11}\text{NO}_2$ . Dopamine is involved in various neurological processes

that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.

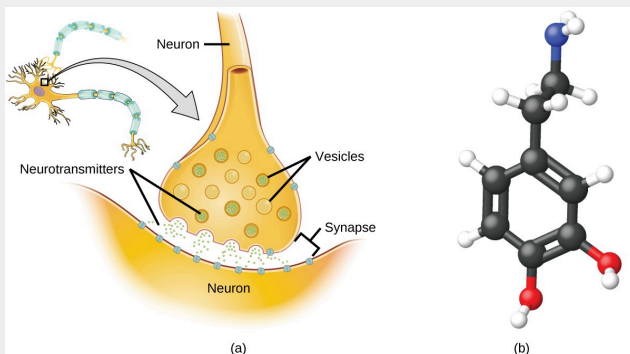


Figure 9. (a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine,  $C_8H_{11}NO_2$ , is a neurotransmitter involved in a number of neurological processes.

One important aspect of the complex processes related to dopamine signaling 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  $5 \times 10^{-20}$  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.<sup>1</sup>

1. Omiatsek, 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

## *Key Concepts and Summary*

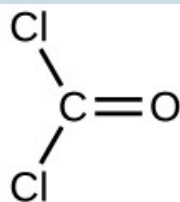
The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molecular mass. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be  $6.022 \times 10^{23}$ , a quantity called Avogadro's number. The mass in grams of 1 mole of 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<sub>2</sub>O molecule weighs approximately 18 amu and 1 mole of H<sub>2</sub>O molecules weighs approximately 18 g).

Cytometry.” *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

## Exercises

- What is the total mass (amu) of carbon in each of the following molecules?
  - $\text{CH}_4$
  - $\text{CHCl}_3$
  - $\text{C}_{12}\text{H}_{10}\text{O}_6$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- What is the total mass of hydrogen in each of the molecules?
  - $\text{CH}_4$
  - $\text{CHCl}_3$
  - $\text{C}_{12}\text{H}_{10}\text{O}_6$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- Calculate the molecular or formula mass of each of the following:
  - $\text{P}_4$
  - $\text{H}_2\text{O}$
  - $\text{Ca}(\text{NO}_3)_2$
  - $\text{CH}_3\text{CO}_2\text{H}$  (acetic acid)
  - $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (sucrose, cane sugar).
- Determine the molecular mass of the following compounds:

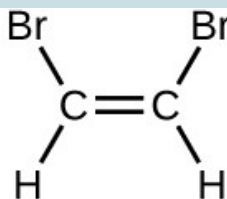
a.



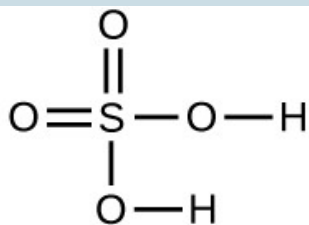
b.



c.

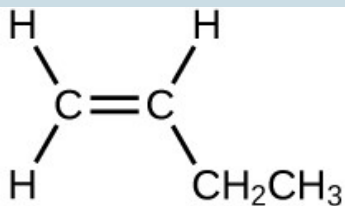


d.

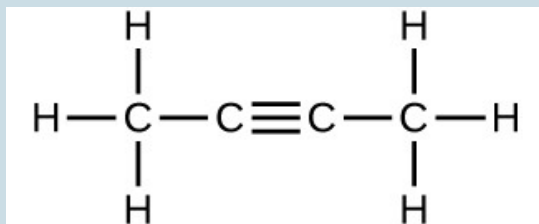


5. Determine the molecular mass of the following compounds:

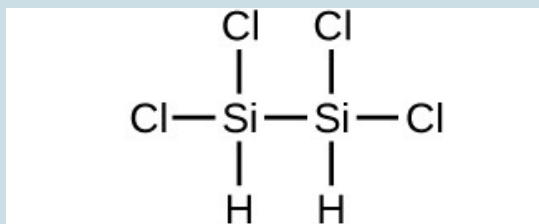
a.



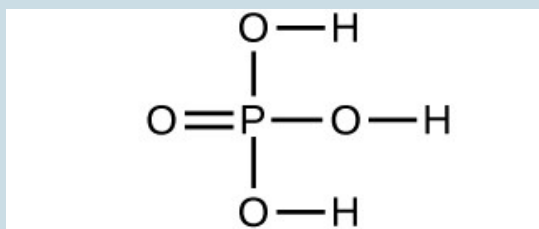
b.



c.



d.

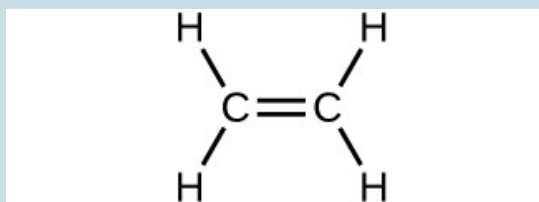


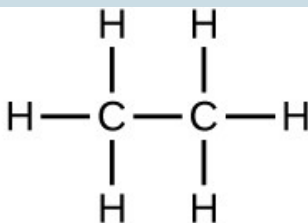
6. Which molecule has a molecular mass of 28.05 amu?

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.
8. Compare 1 mole of  $\text{H}_2$ , 1 mole of  $\text{O}_2$ , and 1 mole of  $\text{F}_2$ .
  - 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 ( $\text{C}_2\text{H}_5\text{OH}$ ), 0.60 mol of formic acid ( $\text{HCO}_2\text{H}$ ), or 1.0 mol of water ( $\text{H}_2\text{O}$ )? Explain why.
10. Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), 1 mol of formic acid ( $\text{HCO}_2\text{H}$ ), or 1 mol of water ( $\text{H}_2\text{O}$ )? Explain why.
11. How are the molecular mass and the molar mass of a compound similar and how are they different?
12. Calculate the molar mass of each of the following compounds:
  - a. hydrogen fluoride,  $\text{HF}$
  - b. ammonia,  $\text{NH}_3$
  - c. nitric acid,  $\text{HNO}_3$
  - d. silver sulfate,  $\text{Ag}_2\text{SO}_4$

- e. boric acid,  $\text{B}(\text{OH})_3$
13. Calculate the molar mass of each of the following:
- $\text{S}_8$
  - $\text{C}_5\text{H}_{12}$
  - $\text{Sc}_2(\text{SO}_4)_3$
  - $\text{CH}_3\text{COCH}_3$  (acetone)
  - $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose)
14. Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:
- limestone,  $\text{CaCO}_3$
  - halite,  $\text{NaCl}$
  - beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
  - malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$
  - turquoise,  $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8(\text{H}_2\text{O})_4$
15. Calculate the molar mass of each of the following:
- the anesthetic halothane,  $\text{C}_2\text{HBrClF}_3$
  - the herbicide paraquat,  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Cl}_2$
  - caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
  - urea,  $\text{CO}(\text{NH}_2)_2$
  - a typical soap,  $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{Na}$
16. Determine the number of moles of compound and the number of moles of each type of atom in each of the following:
- 25.0 g of propylene,  $\text{C}_3\text{H}_6$
  - $3.06 \times 10^{-3}$  g of the amino acid glycine,  $\text{C}_2\text{H}_5\text{NO}_2$
  - 25 lb of the herbicide Treflan,  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4\text{F}$  (1

- lb = 454 g)
- d. 0.125 kg of the insecticide Paris Green,  
 $\text{Cu}_4(\text{AsO}_3)_2(\text{CH}_3\text{CO}_2)_2$
  - e. 325 mg of aspirin,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2\text{CH}_3)$
17. Determine the mass of each of the following:
- a. 0.0146 mol KOH
  - b. 10.2 mol ethane,  $\text{C}_2\text{H}_6$
  - c.  $1.6 \times 10^{-3}$  mol  $\text{Na}_2\text{SO}_4$
  - d.  $6.854 \times 10^3$  mol glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$
  - e. 2.86 mol  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$
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,  $\text{H}_3\text{PO}_4$
  - c. 23 kg of calcium carbonate,  $\text{CaCO}_3$
  - d. 78.452 g of aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$
  - e. 0.1250 mg of caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
19. Determine the mass of each of the following:
- a. 2.345 mol LiCl
  - b. 0.0872 mol acetylene,  $\text{C}_2\text{H}_2$
  - c.  $3.3 \times 10^{-2}$  mol  $\text{Na}_2\text{CO}_3$
  - d.  $1.23 \times 10^3$  mol fructose,  $\text{C}_6\text{H}_{12}\text{O}_6$
  - e. 0.5758 mol  $\text{FeSO}_4(\text{H}_2\text{O})_7$
20. The approximate minimum daily dietary requirement of the amino acid leucine,  $\text{C}_6\text{H}_{13}\text{NO}_2$ , is 1.1 g. What is this requirement in moles?



21. Determine the mass in grams of each of the following:
- 0.600 mol of oxygen atoms
  - 0.600 mol of oxygen molecules,  $O_2$
  - 0.600 mol of ozone molecules,  $O_3$
22. A 55-kg woman has  $7.5 \times 10^{-3}$  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.
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  $Al_2Cl_6$ , or 225 g of  $Al_2S_3$ .
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?
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?

30. A tube of toothpaste contains 0.76 g of sodium monofluorophosphate ( $Na_2PO_3F$ ) in 100 mL
- What mass of fluorine atoms in mg was present?
  - How many fluorine atoms were present?
31. Which of the following represents the least number of molecules?
- 20.0 g of  $H_2O$  (18.02 g/mol)
  - 77.0 g of  $CH_4$  (16.06 g/mol)
  - 68.0 g of  $CaH_2$  (42.09 g/mol)
  - 100.0 g of  $N_2O$  (44.02 g/mol)
  - 84.0 g of  $HF$  (20.01 g/mol)

Show Selected Answers

1. Each molecule has the following mass (amu) of carbon.

- $1 \times 12.01 \text{ amu} = 12.01 \text{ amu}$
- $1 \times 12.01 \text{ amu} = 12.01 \text{ amu}$
- $12 \times 12.01 \text{ amu} = 144.12 \text{ amu}$
- $5 \times 12.01 \text{ amu} = 60.05 \text{ amu}$

3. The molecular or formula masses are as follows:

- $4 \times 30.974 \text{ amu} = 123.896 \text{ amu}$
- $2 \times 1.008 \text{ amu} + 15.999 \text{ amu} = 18.015 \text{ amu}$
- $40 \times 0.078 \text{ amu} + 2 \times 14.007 \text{ amu} + 6 \times 15.999 \text{ amu} = 164.086 \text{ amu}$
- $2 \times 12.011 \text{ amu} + 4 \times 1.008 \text{ amu} + 2 \times 15.999 \text{ amu} = 60.052 \text{ amu}$
- $12 \times 12.011 \text{ amu} + 22 \times 1.008 \text{ amu} + 11 \times 15.999 \text{ amu} = 342.297 \text{ amu}$

5. The molecular mass of each compound is as follows:

a.  $\text{C}_4\text{H}_8$

$$4\text{C} \times 12.011 = 48.044\text{amu}$$

$$8\text{H} \times 1.0079 = \underline{8.06352\text{amu}}$$

$$= 56.107\text{amu}$$

b.  $\text{C}_4\text{H}_6$

$$4\text{C} \times 12.011 = 48.044\text{amu}$$

$$6\text{H} \times 1.0079 = \underline{6.0474\text{amu}}$$

$$= 54.091\text{amu}$$

c.  $\text{H}_2\text{Si}_2\text{Cl}_4$

$$2\text{H} \times 1.0079 = 2.01558\text{amu}$$

$$2\text{Si} \times 28.0855 = 56.1710\text{amu}$$

$$4\text{Cl} \times 35.4527 = \underline{141.8108\text{amu}}$$

$$= 199.9976\text{amu}$$

d.  $\text{H}_3\text{PO}_4$

$$3\text{H} \times 1.0079 = 3.0237\text{amu}$$

$$1\text{P} \times 30.973762 = 30.973762\text{amu}$$

$$4\text{O} \times 15.9994 = \underline{63.9976\text{amu}}$$

$$= 97.9950\text{amu}$$

7. 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.

9. 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.

11. 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

$6.022 \times 10^{23}$  molecules.

13. The molecular mass of each compound is as follows:

a. S<sub>8</sub>:

$$8\text{S} = 8 \times 32.066 = 256.528\text{g/mol}$$

b. C<sub>5</sub>H<sub>12</sub>:

$$5\text{C} = 5 \times 12.011 = 60.055\text{g mol}^{-1}$$

$$12\text{H} = 12 \times 1.00794 = \underline{12.09528\text{g mol}^{-1}}$$

$$= 72.150\text{g mol}^{-1}$$

c. Sc<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>:

$$2\text{Sc} = 2 \times 44.9559109 = 89.9118218\text{g mol}^{-1}$$

$$3\text{S} = 3 \times 32.066 = 96.198\text{g mol}^{-1}$$

$$12\text{O} = 12 \times 15.99943 = \underline{191.99316\text{g mol}^{-1}}$$

$$= 378.103\text{g mol}^{-1}$$

d. CH<sub>3</sub>COCH<sub>3</sub>:

$$3\text{C} = 3 \times 12.011 = 36.033\text{g mol}^{-1}$$

$$1\text{O} = 1 \times 15.9994 = 15.9994\text{g mol}^{-1}$$

$$6\text{H} = 6 \times 1.00794 = \underline{6.04764\text{g mol}^{-1}}$$

$$= 58.080\text{g mol}^{-1}$$

e. C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>:

$$6\text{C} = 6 \times 12.011 = 72.066\text{g mol}^{-1}$$

$$12\text{H} = 12 \times 1.00794 = 12.09528\text{g mol}^{-1}$$

$$6\text{O} = 6 \times 15.9994 = \underline{95.9964\text{g mol}^{-1}}$$

$$= 180.158\text{g mol}^{-1}$$

15. The molecular mass of each compound is as follows:

a.  $\text{C}_2\text{HBrClF}_3$ :

$$2\text{C} = 2 \times 12.011 = 24.022\text{g mol}^{-1}$$

$$1\text{H} = 1 \times 1.00794 = 1.00794\text{g mol}^{-1}$$

$$1\text{Br} = 1 \times 79.904 = 79.904\text{g mol}^{-1}$$

$$1\text{Cl} = 1 \times 35.453 = 35.453\text{g mol}^{-1}$$

$$3\text{F} = 3 \times 18.998403 = \underline{56.995209\text{g mol}^{-1}}$$

$$= 197.682\text{g mol}^{-1}$$

b.  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Cl}_2$ :

$$12\text{C} = 12 \times 12.011 = 144.132\text{g mol}^{-1}$$

$$14\text{H} = 14 \times 1.00794 = 14.111\text{g mol}^{-1}$$

$$2\text{N} = 2 \times 14.0067 = 28.0134\text{g mol}^{-1}$$

$$2\text{Cl} = 2 \times 35.453 = \underline{70.906\text{g mol}^{-1}}$$

$$= 257.163\text{g mol}^{-1}$$

c.  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ :

$$8\text{C} = 8 \times 12.011 = 96.088\text{g mol}^{-1}$$

$$10\text{H} = 10 \times 1.007 = 10.079\text{g mol}^{-1}$$

$$4\text{N} = 4 \times 14.0067 = 56.027\text{g mol}^{-1}$$

$$2\text{O} = 2 \times 15.9994 = \underline{31.999\text{g mol}^{-1}}$$

$$= 194.193\text{g mol}^{-1}$$

d.  $\text{CO}(\text{NH}_2)_2$ :

$$\begin{aligned}
 1\text{C} &= 1 \times 12.011 &= 12.011\text{gmol}^{-1} \\
 1\text{O} &= 1 \times 15.9994 &= 15.9994\text{gmol}^{-1} \\
 2\text{N} &= 2 \times 14.0067 &= 28.0134\text{gmol}^{-1} \\
 4\text{H} &= 4 \times 1.00794 &= 4.03176\text{gmol}^{-1} \\
 &&= \underline{60.056\text{gmol}^{-1}}
 \end{aligned}$$

e.  $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{Na}$ :

$$\begin{aligned}
 18\text{C} &= 18 \times 12.011 &= 216.198\text{gmol}^{-1} \\
 35\text{H} &= 35 \times 1.00794 &= 35.2779\text{gmol}^{-1} \\
 2\text{O} &= 2 \times 15.9994 &= 31.9988\text{gmol}^{-1} \\
 1\text{Na} &= 1 \times 22.98977 &= 22.98977\text{gmol}^{-1} \\
 &&= \underline{306.464\text{gmol}^{-1}}
 \end{aligned}$$

17. The mass of each compound is as follows:

a.  $\text{KOH}$ :

$$\begin{aligned}
 1\text{K} &= 1 \times 39.0983 &= 39.0983 \\
 1\text{O} &= 1 \times 15.9994 &= 15.9994 \\
 1\text{H} &= 1 \times 1.00794 &= \underline{1.00794} \\
 \text{molar mass} &= 56.1056\text{gmol}^{-1} \\
 \text{Mass} &= 0.0146\text{mol} \times 56.1056\text{g/mol} = 0.819\text{g}
 \end{aligned}$$

b.  $\text{C}_2\text{H}_6$ :

$$\begin{aligned}
 2\text{C} &= 2 \times 12.011 &= 24.022 \\
 6\text{H} &= 6 \times 1.00794 &= \underline{6.04764} \\
 \text{molar mass} &= 30.070\text{gmol}^{-1} \\
 \text{Mass} &= 10.2\text{mol} \times 30.070\text{g/mol} = 307\text{g}
 \end{aligned}$$

c.  $\text{Na}_2\text{SO}_4$ :

$$2\text{Na} = 2 \times 22.990 = 45.98$$

$$1\text{S} = 1 \times 32.066 = 32.066$$

$$4\text{O} = 4 \times 15.9994 = \underline{63.9976}$$

$$\text{molar mass} = 142.044\text{g mol}^{-1}$$

$$\text{Mass} = 1.6 \times 10^{-3}\text{mol} \times 142.044\text{g/mol} = 0.23\text{ g}$$

d.  $\text{C}_6\text{H}_{12}\text{O}_6$ :

$$6\text{C} = 6 \times 12.011 = 72.066$$

$$12\text{H} = 12 \times 1.00794 = 12.0953$$

$$6\text{O} = 6 \times 15.9994 = \underline{95.9964}$$

$$\text{molar mass} = 180.158\text{g mol}^{-1}$$

$$\text{Mass} = 6.854 \times 10^3\text{mol} \times 180.158\text{g/mol} = 1.235 \times 10^6\text{ g (1235kg)}$$

e.  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ :

$$\text{Co} = 1 \times 58.99320 = 58.99320$$

$$6\text{N} = 6 \times 14.0067 = 84.0402$$

$$18\text{H} = 18 \times 1.00794 = 18.1429$$

$$3\text{Cl} = 3 \times 35.4527 = \underline{106.358}$$

$$\text{molar mass} = 267.5344\text{g mol}^{-1}$$

$$\text{Mass} = 2.856\text{mol} \times 267.5344\text{g/mol} = 765\text{g}$$

19.

a. 2.345 mol LiCl:

$$\text{molar mass (LiCl)} = 1 \times 6.941 + 1 \times 35.4527 = 42.394\text{g mol}^{-1}$$

$$\text{mass} = 2.345\cancel{\text{mol}} \times 42.394\cancel{\text{g mol}^{-1}} = 99.41\text{g}$$

b. 0.0872 mol acetylene,  $\text{C}_2\text{H}_2$ :

$$\text{molar mass (C}_2\text{H}_2) = 2 \times 12.011 + 2 \times 1.00794 = 26.038\text{g mol}^{-1}$$

$$\text{mass} = 0.0872\cancel{\text{mol}} \times 26.038\cancel{\text{g mol}^{-1}} = 2.27\text{g}$$

c.  $3.3 \times 10^{-2}$  mol  $\text{Na}_2\text{CO}_3$ :

$$\text{molar mass (Na}_2\text{CO}_3) = 2 \times 22.989768 + 1 \times 12.011 + 3 \times 15.9994 = 105.989\text{g mol}^{-1}$$

$$\text{mass} = 3.3 \times 10^{-2}\cancel{\text{mol}} \times 105.989\cancel{\text{g mol}^{-1}} = 3.5\text{g}$$

d.  $1.23 \times 10^3$  mol fructose,  $\text{C}_6\text{H}_{12}\text{O}_6$ :

$$\text{molar mass (C}_6\text{H}_{12}\text{O}_6) = 6 \times 12.011 + 12 \times 1.00794 + 6 \times 15.9994 = 180.158 \text{ g mol}^{-1}$$

$$\text{mass} = 1.23 \times 10^3 \text{ mol} \times 180.158 \text{ g mol}^{-1} = 2.22 \times 10^5 \text{ g} = 222 \text{ kg}$$

e. 0.5758 mol  $\text{FeSO}_4(\text{H}_2\text{O})_7$ :

$$\text{molar mass } [\text{FeSO}_4(\text{H}_2\text{O})_7] = 1 \times 55.847 + 1 \times 32.066 + 4 \times 15.999$$

$$+ 7(2 \times 1.00794 + 15.9994) = 278.018 \text{ g mol}^{-1}$$

$$\text{mass} = 0.5758 \text{ mol} \times 278.018 \text{ g mol}^{-1} = 160.1 \text{ g}$$

21. The mass of each compound is as follows:

a.  $0.600 \text{ mol} \times 15.9994 \text{ g/mol} = 9.60 \text{ g}$

b.  $0.600 \text{ mol} \times 2 \times 15.994 \text{ g/mol} = 19.2 \text{ g}$

c.  $0.600 \text{ mol} \times 3 \times 15.994 \text{ g/mol} = 28.8 \text{ g}$

23. Determine the number of moles of each component.

From the moles, calculate the number of atoms and the mass of the elements involved. Zirconium:

$$0.3384 \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 2.038 \times 10^{23} \text{ atoms}; 0.3384 \text{ mol} \times 91.224 \text{ g/mol} = 30.87 \text{ g};$$

Silicon:

$$0.3384 \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 2.038 \times 10^{23} \text{ atoms}; 0.3384 \text{ mol} \times 28.0855 \text{ g/mol} = 9.504 \text{ g};$$

Oxygen:

$$4 \times 0.3384 \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 8.151 \times 10^{23} \text{ atoms}; 4 \times 0.3384 \text{ mol} \times 15.9994 \text{ g/mol} = 21.66 \text{ g}$$

25. Determine the molar mass and, from the grams present, the moles of each substance. The compound with the greatest number of moles of Al has the greatest mass of Al.

- Molar mass  $\text{AlPO}_4$ :  $26.981539 + 30.973762 + 4(15.9994) = 121.9529 \text{ g/mol}$
- Molar mass  $\text{Al}_2\text{Cl}_6$ :  $2(26.981539) + 6(35.4527) = 266.6793 \text{ g/mol}$
- Molar mass  $\text{Al}_2\text{S}_3$ :  $2(26.981539) + 3(32.066) = 150.161 \text{ g/mol}$



$$\text{AlPO}_4: \frac{122 \cancel{\text{g}}}{121.9529 \cancel{\text{g}} \text{mol}^{-1}} = 1.000 \text{mol.}$$

$$\text{mol Al} = 1 \times 1.000 \text{mol} = 1.000 \text{mol}$$

$$\text{Al}_2\text{Cl}_6: \frac{266 \text{g}}{266.6793 \text{gmol}^{-1}} = 0.997 \text{mol}$$

$$\text{mol Al} = 2 \times 0.997 \text{mol} = 1.994 \text{mol}$$

$$\text{Al}_2\text{S}_3: \frac{225 \cancel{\text{g}}}{150.161 \cancel{\text{g}} \text{mol}^{-1}} = 1.50 \text{mol}$$

$$\text{mol Al} = 2 \times 1.50 \text{mol} = 3.00 \text{mol}$$

27. Determine the number of grams present in the diamond and from that the number of moles. Find the number of carbon atoms by multiplying Avogadro's number by the number of moles:

$$\frac{3104 \cancel{\text{carats}} \times \frac{200 \cancel{\text{mg}}}{1 \cancel{\text{carat}}} \times \frac{1 \cancel{\text{g}}}{1000 \cancel{\text{mg}}}}{12.011 \cancel{\text{g}} \text{mol}^{-1} (6.022 \times 10^{23} \cancel{\text{mol}^{-1}})} = 3.113 \times 10^{25} \text{C atoms}$$

29. Determine the molar mass of sugar,  $12(12.011) + 22(1.00794) + 11(15.9994) = 342.300 \text{ g/mol}$ ; Then  
 $0.0278 \text{mol} \times 342.300 \text{g/mol} = 9.52 \text{g sugar.}$

This 9.52 g of sugar represents  $\frac{11.0}{60.0}$  of one serving or

$$\frac{60.0 \text{g serving}}{11.0 \cancel{\text{g sugar}}} \times 9.52 \cancel{\text{g sugar}} = 51.9 \text{g cereal.}$$

This amount is  $\frac{51.9 \text{g cereal}}{60.0 \text{g serving}} = 0.865$  servings,  
 or about 1 serving.

31. Calculate the number of moles of each species, then

remember that 1 mole of anything =  $6.022 \times 10^{23}$  species.

- a. 20.0 g = 1.11 mol H<sub>2</sub>O
- b. 77.0 g CH<sub>4</sub> = 4.79 mol CH<sub>4</sub>
- c. 68.0 g CaH<sub>2</sub> = 1.62 mol CaH<sub>2</sub>
- d. 100.0 g N<sub>2</sub>O = 2.27 mol N<sub>2</sub>O
- e. 84.0 g HF = 4.20 mol HF

Therefore, 20.0 g H<sub>2</sub>O represents the least number of molecules since it has the least number of moles.

## Glossary

**Avogadro's number ( $N_A$ ):** experimentally determined value of the number of entities comprising 1 mole of substance, equal to  $6.022 \times 10^{23} \text{mol}^{-1}$

**formula mass:** sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

**molar mass:** mass in grams of 1 mole of a substance

**mole:** amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of <sup>12</sup>C

## 37. 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



*Figure 1. 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: Jane Whitney)*

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 1). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.

## 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 liter (1 L) of the solution:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

### *Example 1: Calculating Molar Concentrations*

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Show Answer

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133\text{mol}}{355\text{mL} \times \frac{1\text{L}}{1000\text{mL}}} = 0.375M$$

### *Check Your Learning*

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?

Show Answer

0.05 M

### *Example 2: Deriving Moles and Volumes from Molar Concentrations*

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 1?

Show Answer

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 1, 0.375 M:

$$\begin{aligned}M &= \frac{\text{mol solute}}{\text{L solution}} \\ \text{mol solute} &= M \times \text{L solution} \\ \text{mol solute} &= 0.375 \frac{\text{mol sugar}}{\text{L}} \times \left(10\text{mL} \times \frac{1\text{L}}{1000\text{mL}}\right) = 0.004\text{mol sugar}\end{aligned}$$

### *Check Your Learning*

What volume (mL) of the sweetened tea described in Example 1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Show Answer

80 mL

### *Example 3: Calculating Molar Concentrations*

## *from the Mass of Solute*

Distilled white vinegar (Figure 2) is a solution of acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , 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 2. Distilled white vinegar is a solution of acetic acid in water.

Show Answer

As in previous examples, 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:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\text{gCH}_2\text{CO}_2\text{H} \times \frac{1\text{mol CH}_2\text{CO}_2\text{H}}{60.052\text{g CH}_2\text{CO}_2\text{H}}}{0.500\text{ L solution}} = 0.839M$$

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839M$$

$$M = \frac{0.839\text{mol solute}}{1.00\text{L solution}}$$

### *Check Your Learning*

Calculate the molarity of 6.52 g of  $\text{CoCl}_2$  (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Show Answer

0.674 M

### *Example 4: Determining the Mass of Solute in a Given Volume of Solution*

How many grams of  $\text{NaCl}$  are contained in 0.250 L of a 5.30-M solution?

Show Answer

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 2:



$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 5.30 \frac{\text{mol NaCl}}{\text{L}} \times 0.250\text{L} = 1.325\text{mol NaCl}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325 \text{ mol NaCl} \times \frac{58.44\text{g NaCl}}{\text{mol NaCl}} = 77.4\text{g NaCl}$$

### *Check Your Learning*

How many grams of  $\text{CaCl}_2$  (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

Show Answer

5.55 g  $\text{CaCl}_2$

When performing calculations stepwise, 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 5). This eliminates intermediate steps so that only the final result is rounded.

### *Example 5: Determining the Volume of Solution Containing a Given Mass of Solute*

In Example 3, we found the typical concentration of vinegar to be 0.839 M. What volume of vinegar contains 75.6 g of acetic acid?

Show Answer

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:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$
$$75.6\text{gCH}_3\text{CO}_2\text{H} \left( \frac{\text{molCH}_3\text{CO}_2\text{H}}{60.05\text{g}} \right) \left( \frac{\text{L solution}}{0.839\text{molCH}_3\text{CO}_2\text{H}} \right) = 1.50\text{L solution}$$

### *Check Your Learning*

What volume of a 1.50-M KBr solution contains 66.0 g KBr?

Show Answer

0.370 L

## 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

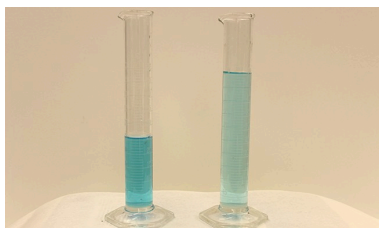


Figure 3. Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)

solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 3).

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 4).

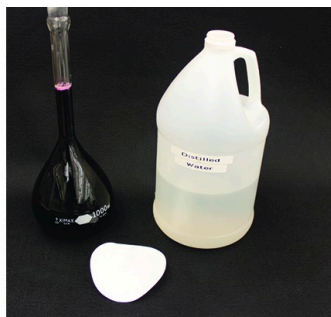


Figure 4. A solution of  $\text{KMnO}_4$  is prepared by mixing water with 4.74 g of  $\text{KMnO}_4$  in a flask. (credit: modification of work by Mark Ott)

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 liters:  $n = ML$ .

Expressions like these may be written for a solution before and after it is diluted:

$$\begin{aligned}n_1 &= M_1L_1 \\ n_2 &= M_2L_2\end{aligned}$$

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 liters 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.

Use the [PhET simulation for Concentration](#) to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

### *Example 6: Determining the Concentration of a Diluted Solution*

If 0.850 L of a 5.00-M solution of copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Show Answer

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  $C_2$ :

$$C_1 V_1 = C_2 V_2$$
$$C_2 = \frac{C_1 V_1}{V_2}$$

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:

$$C_2 = \frac{0.850\text{L} \times 5.00 \frac{\text{mol}}{\text{L}}}{1.80\text{L}} = 2.36\text{M}$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 M).

### *Check Your Learning*

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of  $\text{CH}_3\text{OH}$  to 500.0 mL?

Show Answer

0.102 M  $\text{CH}_3\text{OH}$

### *Example 7: 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?

Show Answer

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  $V_2$ :

$$C_1 V_1 = C_2 V_2$$

$$V_2 = \frac{C_1 V_1}{C_2}$$

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 concentration, or around 44

mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45M)(0.011L)}{(0.12M)}$$
$$V_2 = 0.041L$$

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.

### *Check Your Learning*

A laboratory experiment calls for 0.125 M  $\text{HNO}_3$ . What volume of 0.125 M  $\text{HNO}_3$  can be prepared from 0.250 L of 1.88 M  $\text{HNO}_3$ ?

Show Answer

3.76 L

### *Example 8: 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?

Show Answer

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  $V_1$ :

$$C_1 V_1 = C_2 V_2$$
$$V_1 = \frac{C_2 V_2}{C_1}$$

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 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100M)(5.00L)}{1.59M}$$
$$V_1 = 0.314L$$

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.

### *Check Your Learning*

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?

Show Answer

0.261 L



## *Key Concepts and Summary*

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 liter 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.

### *Key Equations*

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

## *Exercises*

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?
  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  $\text{CoCl}_2$  in 0.654 L of solution
    - b. 98.0 g of phosphoric acid,  $\text{H}_3\text{PO}_4$ , in 1.00 L of solution
    - c. 0.2074 g of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , in 40.00 mL of solution
    - d. 10.5 kg of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in 18.60 L of solution
    - e.  $7.0 \times 10^{-3} \text{ mol}$  of  $\text{I}_2$  in 100.0 mL of solution
    - f.  $1.8 \times 10^4 \text{ mg}$  of HCl in 0.075 L of solution
  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  $\text{H}_2\text{SO}_4$  in 1.00 L of solution
    - c. 20.54 g of  $\text{Al}(\text{NO}_3)_3$  in 1575 mL of solution
    - d. 2.76 kg of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 1.45 L of solution
    - e. 0.005653 mol of  $\text{Br}_2$  in 10.00 mL of solution
    - f. 0.000889 g of glycine,  $\text{C}_2\text{H}_5\text{NO}_2$ , 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,  $\text{C}_6\text{H}_{12}\text{O}_6$ , used for intravenous injection?

- a. Outline the steps necessary to answer the question.
  - b. Answer the question.
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  $\text{H}_2\text{SO}_4$ , concentrated sulfuric acid
  - b. 100.0 mL of  $3.8 \times 10^{-5} \text{ M NaCN}$ , the minimum lethal concentration of sodium cyanide in blood serum
  - c. 5.50 L of 13.3 M  $\text{H}_2\text{CO}$ , the formaldehyde used to “fix” tissue samples
  - d. 325 mL of  $1.8 \times 10^{-6} \text{ M FeSO}_4$ , the minimum concentration of iron sulfate detectable by taste in drinking water
9. Calculate the number of moles and the mass of the solute in each of the following solutions:
  - a. 325 mL of  $8.23 \times 10^{-5} \text{ M KI}$ , a source of iodine in the diet
  - b. 75.0 mL of  $2.2 \times 10^{-5} \text{ M H}_2\text{SO}_4$ , a

- sample of acid rain
- c. 0.2500 L of 0.1135 M  $\text{K}_2\text{CrO}_4$ , an analytical reagent used in iron assays
  - d. 10.5 L of 3.716 M  $(\text{NH}_4)_2\text{SO}_4$ , a liquid fertilizer
10. Consider this question: What is the molarity of  $\text{KMnO}_4$  in a solution of 0.0908 g of  $\text{KMnO}_4$  in 0.500 L of solution?
- a. Outline the steps necessary to answer the question.
  - b. Answer the question.
11. Consider this question: What is the molarity of  $\text{HCl}$  if 35.23 mL of a solution of  $\text{HCl}$  contain 0.3366 g of  $\text{HCl}$ ?
- 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,  $\text{C}_{27}\text{H}_{46}\text{O}$ , in 0.100 L of serum, the average concentration of cholesterol in human serum
  - b. 4.25 g of  $\text{NH}_3$  in 0.500 L of solution, the concentration of  $\text{NH}_3$  in household ammonia
  - c. 1.49 kg of isopropyl alcohol,  $\text{C}_3\text{H}_7\text{OH}$ , in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol
  - d. 0.029 g of  $\text{I}_2$  in 0.100 L of solution, the solubility of  $\text{I}_2$  in water at 20 °C

13. Calculate the molarity of each of the following solutions:
- 293 g HCl in 666 mL of solution, a concentrated HCl solution
  - 2.026 g  $\text{FeCl}_3$  in 0.1250 L of a solution used as an unknown in general chemistry laboratories
  - 0.001 mg  $\text{Cd}^{2+}$  in 0.100 L, the maximum permissible concentration of cadmium in drinking water
  - 0.0079 g  $\text{C}_7\text{H}_5\text{SNO}_3$  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  $\text{Ca}^{2+}$ , in 1.0 L of milk. What is the molarity of  $\text{Ca}^{2+}$  in milk?
15. What volume of a 1.00-M  $\text{Fe}(\text{NO}_3)_3$  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  $\text{C}_3\text{H}_7\text{OH}$  solution is diluted to a concentration of 0.1222 M, what is the volume of the resulting solution?
17. If 4.12 L of a 0.850 M- $\text{H}_3\text{PO}_4$  solution is be diluted to a volume of 10.00 L, what is the concentration the resulting solution?
18. What volume of a 0.33-M  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 M?
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  $\text{Fe}(\text{NO}_3)_3$  is diluted to a final volume of 2.00 L
  - b. 0.5000 L of a 0.1222-M solution of  $\text{C}_3\text{H}_7\text{OH}$  is diluted to a final volume of 1.250 L
  - c. 2.35 L of a 0.350-M solution of  $\text{H}_3\text{PO}_4$  is diluted to a final volume of 4.00 L
  - d. 22.50 mL of a 0.025-M solution of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  is diluted to 100.0 mL
21. What is the final concentration of the solution produced when 225.5 mL of a 0.09988-M solution of  $\text{Na}_2\text{CO}_3$  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?
  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  $\text{K}_2\text{SO}_4$  solution contains 57 g of  $\text{K}_2\text{SO}_4$ ?
  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 ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), what is the maximum permissible molarity of that

substance?

Show Selected Answers

2. We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

4. The molarity of each solution is as follows:

a. 
$$\frac{0.444\text{mol}}{0.654\text{L}} = 0.679\text{mol L}^{-1} = 0.679M$$

b. First convert mass in grams to moles, and then substitute the proper terms into the definition.

Molar mass of  $\text{H}_3\text{PO}_4 = 97.995 \text{ g/mol}$

$$\text{mol}(\text{H}_3\text{PO}_4) = 98.0\text{g} \times \frac{1\text{mol}}{97.995\text{g}} = 1.00\text{mol}$$

$$M = \frac{1.00\text{mol}}{1.00\text{L}} = 1.00M$$

c. Molar mass  $[\text{Ca}(\text{OH})_2] = 79.09 \text{ g/mol}$

$$0.2074\cancel{\text{g}} \times \frac{1\text{mol}}{79.09\cancel{\text{g}}} = 0.002799\text{molCa}(\text{OH})_2$$

$$\frac{0.002799\text{mol}}{0.0400\text{L}} = 0.06998\text{mol L}^{-1} = 0.06998M$$

d. Molar mass  $(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}) = 322.20 \text{ g/mol}$

$$10,500 \times \frac{1\text{mol}}{322.20\text{g}} = 32.6\text{mol}$$

$$\frac{32.6\text{mol}}{18.60\text{L}} = 1.75M$$

e. 
$$M = \frac{\text{millimoles solute}}{\text{volume of solution in milliliters}}$$

$$\frac{7.00 \text{ mmol I}_2}{100 \text{ mL}} = 0.070M$$

f. Molar mass  $(\text{HCl}) = 36.46 \text{ g/mol}$

$$\text{mass (HCl)} = 1.8 \times 10^1 \text{ g HCl} \times \frac{1 \text{ mol}}{36.46 \text{ g}} = 0.49 \text{ mol HCl}$$

$$\frac{0.49 \text{ mol HCl}}{0.075 \text{ L}} = 6.6M$$

6. The answers are as follows:

- 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;

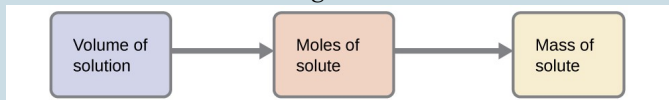
- b. 0.500 L contains

$$0.30M \times 0.500L = 1.5 \times 10^{-1} \text{ mol.}$$

Molar mass (glucose):

$$6 \times 12.0011 \text{ g} + 12 \times 1.00794 \text{ g} + 6 \times 15.9994 \text{ g} = 180.158 \text{ g}, 1.5 \times 10^{-1} \text{ mol} \times 180.158 \text{ g/mol} = 27 \text{ g.}$$

8. The molarity must be converted to moles of solute, which is then converted to grams of solute:



$$M = \frac{\text{mol}}{\text{liter}} \quad \text{or} \quad \text{mol} = M \times \text{liter}$$

a.  $\text{mol H}_2\text{SO}_4 = 2.00 \cancel{\text{L}} \times \frac{18.5 \text{ mol}}{\cancel{\text{L}}} = 37.0 \text{ mol H}_2\text{SO}_4$

$$37.0 \cancel{\text{mol H}_2\text{SO}_4} \times \frac{98.08 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} = 3.63 \times 10^3 \text{ g H}_2\text{SO}_4$$

b.  $\text{mol NaCN} = 0.1000 \cancel{\text{L}} \times \frac{3.8 \times 10^{-5} \text{ mol}}{\cancel{\text{L}}} = 3.8 \times 10^{-6} \text{ mol NaCN}$

$$3.8 \times 10^{-6} \cancel{\text{mol NaCN}} \times \frac{49.01 \text{ g}}{1 \text{ mol NaCN}} = 1.9 \times 10^{-4} \text{ g NaCN}$$



$$\begin{aligned} \text{c.} \quad \text{mol H}_2\text{CO} &= 5.50 \cancel{\text{L}} \times \frac{13.3 \cancel{\text{mol}}}{\cancel{\text{L}}} = 73.2 \text{ mol H}_2\text{CO} \\ 73.2 \cancel{\text{mol H}_2\text{CO}} &\times \frac{30.026 \text{ g}}{1 \cancel{\text{mol H}_2\text{CO}}} = 2198 \text{ g H}_2\text{CO} = 2.20 \text{ kg H}_2\text{CO} \\ \text{d.} \quad \text{mol FeSO}_4 &= 0.325 \cancel{\text{L}} \times \frac{1.8 \times 10^{-6} \cancel{\text{mol}}}{\cancel{\text{L}}} = 5.9 \times 10^{-7} \text{ mol FeSO}_4 \\ 5.85 \times 10^{-7} \cancel{\text{mol FeSO}_4} &\times \frac{151.9 \text{ g}}{1 \cancel{\text{mol FeSO}_4}} = 8.9 \times 10^{-5} \text{ g FeSO}_4 \end{aligned}$$

10. The answers are as follows:

- Determine the molar mass of  $\text{KMnO}_4$ ; determine the number of moles of  $\text{KMnO}_4$  in the solution; from the number of moles and the volume of solution, determine the molarity
- Molar mass of  $\text{KMnO}_4 = 158.0264 \text{ g/mol}$

$$\begin{aligned} \text{mol KMnO}_4 &= 0.0908 \cancel{\text{g KMnO}_4} \times \frac{1 \text{ mol}}{158.0264 \text{ g KMnO}_4} = 5.746 \times 10^{-4} \text{ mol} \\ M \text{KMnO}_4 &= \frac{5.746 \times 10^{-4} \cancel{\text{mol}}}{0.500 \text{ L}} = 1.15 \times 10^{-3} M \end{aligned}$$

12. The molarity for each solution is as follows:

$$\begin{aligned} \text{a.} \quad M \text{C}_{27}\text{H}_{46}\text{O} &= \frac{\text{mol}}{V} = \frac{\frac{0.195 \cancel{\text{g C}_{27}\text{H}_{46}\text{O}}}{386.660 \cancel{\text{g mol}^{-1} \text{C}_{27}\text{H}_{46}\text{O}}}}{\frac{0.100 \text{ L}}{4.25 \cancel{\text{g NH}_3}}} = 5.04 \times 10^{-3} M \\ \text{b.} \quad M \text{NH}_3 &= \frac{\text{mol}}{V} = \frac{\frac{17.0304 \cancel{\text{g mol}^{-1} \text{NH}_3}}{0.500 \text{ L}}}{4.25 \cancel{\text{g NH}_3}} = 0.499 M \\ \text{c.} \quad M \text{C}_3\text{H}_7\text{OH} &= \frac{\text{mol}}{V} = \frac{1.49 \cancel{\text{kg C}_3\text{H}_7\text{OH}} \times \frac{1000 \cancel{\text{g}}}{1 \cancel{\text{kg}}} \times \frac{1 \text{ mol C}_3\text{H}_7\text{OH}}{60.096 \cancel{\text{g}}}}{\frac{0.029 \cancel{\text{g I}_2}}{2.50 \text{ L}}} = 9.92 M \\ \text{d.} \quad M \text{I}_2 &= \frac{\text{mol}}{V} = \frac{\frac{253.8090 \cancel{\text{g mol}^{-1} \text{I}_2}}{0.100 \text{ L}}}{1.0 \cancel{\text{g}}} = 1.1 \times 10^{-3} M \\ \text{14.} \quad M &= \frac{\text{mol}}{V} = \frac{\frac{40.08 \cancel{\text{g mol}^{-1}}}{1.0 \text{ L}}}{1.0 \cancel{\text{g}}} = 0.025 M \end{aligned}$$

$$\frac{C_1 V_1}{C_2} = V_2$$

$$16. \frac{\frac{0.3556 \text{ mol}}{\text{L}} \times 0.1718 \text{ L}}{\frac{0.1222 \text{ mol}}{\text{L}}} = V_2$$

$$0.5000 \text{ L} = V_2$$

18.

$$V_1 = \frac{V_2 \times M_2}{M_1} = 25 \text{ mL} \times \frac{0.025 \text{ M}}{0.33 \text{ M}} = 1.9 \text{ mL}$$

20. The molarity for each diluted solution is as follows:

$$\text{a. } C_2 = \frac{V_1 \times C_1}{V_2} = 1.00 \cancel{\text{ L}} \times \frac{0.250 \text{ M}}{2.00 \cancel{\text{ L}}} = 0.125 \text{ M}$$

$$\text{b. } C_2 = \frac{V_1 \times C_1}{V_2} = 0.5000 \cancel{\text{ L}} \times \frac{0.1222 \text{ M}}{1.250 \cancel{\text{ L}}} = 0.04888 \text{ M}$$

$$\text{c. } C_2 = \frac{V_1 \times C_1}{V_2} = 2.35 \cancel{\text{ L}} \times \frac{0.350 \text{ M}}{4.00 \cancel{\text{ L}}} = 0.206 \text{ M}$$

$$\text{d. } C_2 = \frac{V_1 \times C_1}{V_2} = 0.02250 \cancel{\text{ mL}} \times \frac{0.025 \text{ M}}{0.100 \cancel{\text{ mL}}} = 0.0056 \text{ M}$$

22. Determine the number of moles in 434.4 g of HCl:

$$1.00794 + 35.4527 = 36.4606 \text{ g/mol}$$

$$\text{mol HCl} = \frac{434.4 \cancel{\text{ g}}}{36.4606 \cancel{\text{ g}} \text{ mol}^{-1}} = 11.91 \text{ mol}$$

This HCl is present in 1.00 L, so the molarity is 11.9 M.

24.

$$57 \text{ g K}_2\text{SO}_4 \times \frac{1 \text{ mol}}{174.26 \text{ g}} \times \frac{1 \text{ L}}{0.20 \text{ mol}} = 1.6 \text{ L}$$

## Glossary

**aqueous solution:** solution for which water is the solvent

**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

**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

**dissolved:** describes the process by which solute components are dispersed in a solvent

**molarity (M):** unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

**solute:** solution component present in a concentration less than that of the solvent

**solvent:** solution component present in a concentration that is higher relative to other components

## 38. Reaction Stoichiometry

### *Learning Objectives*

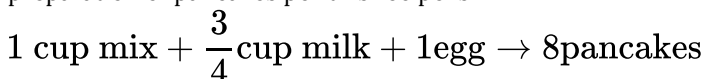
By the end of this section, you will be able to:

- 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
- Perform stoichiometric calculations involving mass, moles, and solution molarity

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

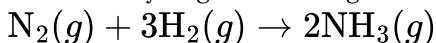
pancake mix,  $\frac{3}{4}$  cup milk, and one egg. The “equation” representing the preparation of pancakes per this recipe is



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

$$\cancel{24 \text{ pancakes}} \times \frac{1 \text{ egg}}{\cancel{8 \text{ pancakes}}} = 3 \text{ eggs}$$

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:



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.

### *Example 1: 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 1)?

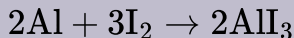
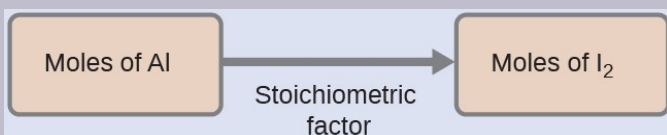


Figure 1. Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Show Answer

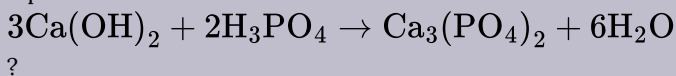
Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is  $\frac{3 \text{ mol } I_2}{2 \text{ mol Al}}$ . The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\begin{aligned}\text{mol I}_2 &= 0.429 \cancel{\text{mol Al}} \times \frac{3 \text{ mol I}_2}{2 \cancel{\text{mol Al}}} \\ &= 0.644 \text{ mol I}_2\end{aligned}$$

### *Check Your Learning*

How many moles of  $\text{Ca}(\text{OH})_2$  are required to react with 1.36 mol of  $\text{H}_3\text{PO}_4$  to produce  $\text{Ca}_3(\text{PO}_4)_2$  according to the equation

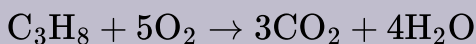


Show Answer

2.04 mol

### *Example 2: Number of Product Molecules Generated by a Reaction*

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?



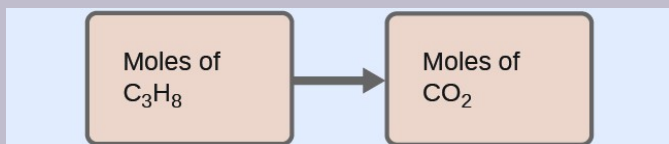
Show Answer

The approach here is the same as for Example 1, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3 \text{ molCO}_2}{1 \text{ molC}_3\text{H}_8}$$

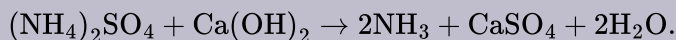
Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75 \cancel{\text{ molC}_3\text{H}_8} \times \frac{3 \cancel{\text{ molCO}_2}}{1 \cancel{\text{ molC}_3\text{H}_8}} \times \frac{6.022 \times 10^{23} \text{ CO}_2 \text{ molecules}}{\cancel{\text{ molCO}_2}} = 1.4 \times 10^{24} \text{ CO}_2 \text{ molecules}$$

### Check Your Learning

How many  $\text{NH}_3$  molecules are produced by the reaction of 4.0 mol of  $\text{Ca(OH)}_2$  according to the following equation:



Show Answer

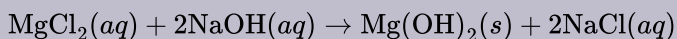
$$4.8 \times 10^{24} \text{ NH}_3 \text{ molecules}$$



These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

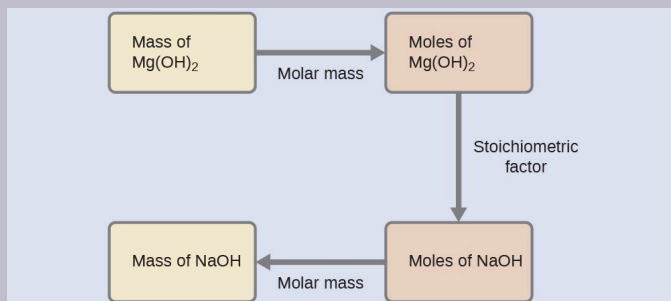
### *Example 3: Relating Masses of Reactants and Products*

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, Mg(OH)<sub>2</sub>] by the following reaction?



Show Answer

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:



$$16 \text{ g } \cancel{\text{Mg(OH)}_2} \times \frac{1 \text{ mol } \cancel{\text{Mg(OH)}_2}}{58.3 \text{ g } \cancel{\text{Mg(OH)}_2}} \times \frac{2 \text{ mol } \cancel{\text{NaOH}}}{1 \text{ mol } \cancel{\text{Mg(OH)}_2}} \times \frac{40.0 \text{ g NaOH}}{\cancel{\text{mol NaOH}}} = 22 \text{ g NaOH}$$

### Check Your Learning

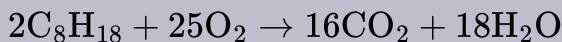
What mass of gallium oxide,  $\text{Ga}_2\text{O}_3$ , can be prepared from 29.0 g of gallium metal? The equation for the reaction is  $4\text{Ga} + 3\text{O}_2 \rightarrow 2\text{Ga}_2\text{O}_3$ .

Show Answer

39.0 g

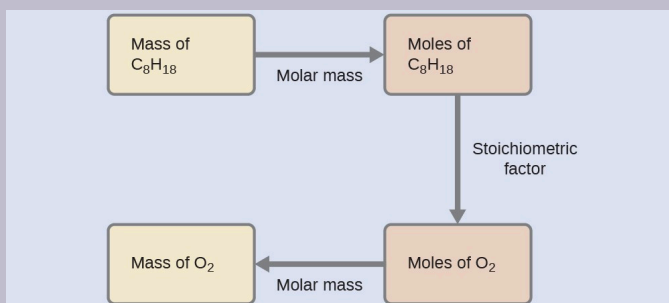
### Example 4: Relating Masses of Reactants

What mass of oxygen gas,  $\text{O}_2$ , from the air is consumed in the combustion of 702 g of octane,  $\text{C}_8\text{H}_{18}$ , one of the principal components of gasoline?



Show Answer

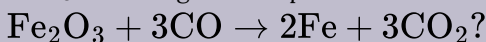
The approach required here is the same as for the Example 3, differing only in that the provided and requested masses are both for reactant species.



$$702 \cancel{\text{gC}_8\text{H}_{18}} \times \frac{1 \cancel{\text{molC}_8\text{H}_{18}}}{114.23 \text{gC}_8\text{H}_{18}} \times \frac{25 \cancel{\text{molO}_2}}{2 \cancel{\text{molC}_8\text{H}_{18}}} \times \frac{32.00 \text{gO}_2}{\cancel{\text{molO}_2}} = 2.46 \times 10^3 \text{gO}_2$$

### Check Your Learning

What mass of CO is required to react with 25.13 g of  $\text{Fe}_2\text{O}_3$  according to the equation



Show Answer

13.22 g

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 2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

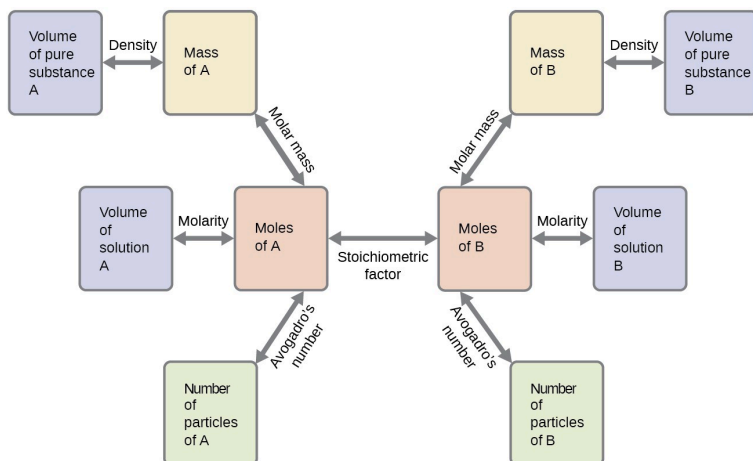


Figure 2. The flow chart depicts the various computational steps involved in most reaction stoichiometry calculations.

## Airbags

Airbags (Figure 3) 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



Figure 3. Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

decomposition of sodium azide,  $\text{NaN}_3$ . When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of  $\text{NaN}_3$  to initiate its decomposition:



This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second ( $\sim 0.03$ – $0.1$  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 ( $\sim 100$  g) of  $\text{NaN}_3$  will generate approximately 50 L of  $\text{N}_2$ .

For more information about the chemistry and physics behind airbags and for helpful diagrams on how airbags work, [go to How Stuff Works' "How Airbags Work" article](#).



### *Key Concepts and Summary*

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.

## Exercises

- Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

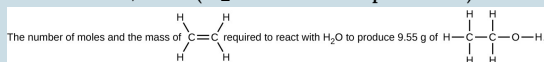
- The number of moles and the mass of chlorine,  $\text{Cl}_2$ , required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.
- The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.
- The number of moles and the mass of sodium nitrate,  $\text{NaNO}_3$ , required to produce 128 g of oxygen. ( $\text{NaNO}_2$  is the other product.)
- 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.
- The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. ( $\text{CO}_2$  is the other product.)

- The number of moles and the mass of  formed by the reaction of 12.85 g of  with an excess of  $\text{Br}_2$ .

- Determine the number of moles and the mass requested for each reaction in Exercise 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 Mg required to react with 5.00 g of HCl and produce  $\text{MgCl}_2$  and  $\text{H}_2$ .
- 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,  $\text{MgCO}_3$ , required to produce 283 g of carbon dioxide. ( $\text{MgO}$  is the other product.)
- d. The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene,  $\text{C}_2\text{H}_2$ , in an excess of oxygen.
- e. The number of moles and the mass of barium peroxide,  $\text{BaO}_2$ , needed to produce 2.500 kg of barium oxide,  $\text{BaO}$  ( $\text{O}_2$  is the other product.)

f.



4. Determine the number of moles and the mass requested for each reaction in Exercise 3.
5.  $\text{H}_2$  is produced by the reaction of 118.5 mL of a 0.8775-M solution of  $\text{H}_3\text{PO}_4$  according to the following equation:  

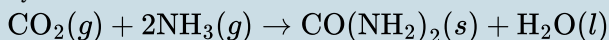
$$2\text{Cr} + 2\text{H}_3\text{PO}_4 \rightarrow 3\text{H}_2 + 2\text{CrPO}_4.$$
  - a. Outline the steps necessary to determine the number of moles and mass of  $\text{H}_2$ .
  - b. Perform the calculations outlined.
6. Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of HCl according to the following equation:  $2\text{Ga} + 6\text{HCl} \rightarrow 2\text{GaCl}_3 + 3\text{H}_2$ .

- a. Outline the steps necessary to determine the number of moles and mass of gallium chloride.
  - b. Perform the calculations outlined.
7.  $\text{I}_2$  is produced by the reaction of 0.4235 mol of  $\text{CuCl}_2$  according to the following equation:  
$$2\text{CuCl}_2 + 4\text{KI} \rightarrow 2\text{CuI} + 4\text{KCl} + \text{I}_2.$$
  - a. How many molecules of  $\text{I}_2$  are produced?
  - b. What mass of  $\text{I}_2$  is produced?
8. Silver is often extracted from ores as  $\text{K}[\text{Ag}(\text{CN})_2]$  and then recovered by the reaction  
$$2\text{K}[\text{Ag}(\text{CN})_2](aq) + \text{Zn}(s) \rightarrow 2\text{Ag}(s) + \text{Zn}(\text{CN})_2(aq) + 2\text{KCN}(aq)$$
  - a. How many molecules of  $\text{Zn}(\text{CN})_2$  are produced by the reaction of 35.27 g of  $\text{K}[\text{Ag}(\text{CN})_2]$ ?
  - b. What mass of  $\text{Zn}(\text{CN})_2$  is produced?
9. What mass of silver oxide,  $\text{Ag}_2\text{O}$ , is required to produce 25.0 g of silver sulfadiazine,  $\text{AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2$ , from the reaction of silver oxide and sulfadiazine?  
$$2\text{C}_{10}\text{H}_9\text{N}_4\text{SO}_2 + \text{Ag}_2\text{O} \rightarrow 2\text{AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2 + \text{H}_2\text{O}$$
10. Carborundum is silicon carbide,  $\text{SiC}$ , a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand,  $\text{SiO}_2$ , with carbon at high temperature. Carbon monoxide,  $\text{CO}$ , is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much  $\text{SiO}_2$  is required to produce 3.00 kg of  $\text{SiC}$ .
11. Automotive air bags inflate when a sample of sodium azide,  $\text{NaN}_3$ , is very rapidly decomposed.



$2\text{NaN}_3(s) \rightarrow 2\text{Na}(s) + 3\text{N}_2(g)$  What mass of sodium azide is required to produce  $2.6 \text{ ft}^3$  ( $73.6 \text{ L}$ ) of nitrogen gas with a density of  $1.25 \text{ g/L}$ ?

12. Urea,  $\text{CO}(\text{NH}_2)_2$ , 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  $\text{CO}_2$  produced by combustion of  $1.00 \times 10^3 \text{ kg}$  of carbon followed by the reaction?



13. In an accident, a solution containing  $2.5 \text{ kg}$  of nitric acid was spilled. Two kilograms of  $\text{Na}_2\text{CO}_3$  was quickly spread on the area and  $\text{CO}_2$  was released by the reaction. Was sufficient  $\text{Na}_2\text{CO}_3$  used to neutralize all of the acid?
14. 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  $0.8205 \text{ g/mL}$ , determine the mass of carbon dioxide produced during a  $500$ -mile trip ( $3.785$  liters per gallon).
15. What volume of a  $0.750 \text{ M}$  solution of hydrochloric acid, a solution of  $\text{HCl}$ , can be prepared from the  $\text{HCl}$  produced by the reaction of  $25.0 \text{ g}$  of  $\text{NaCl}$  with an excess of sulfuric acid?
- $$\text{NaCl}(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{HCl}(g) + \text{NaHSO}_4(s)$$
16. What volume of a  $0.2089 \text{ M}$   $\text{KI}$  solution contains enough  $\text{KI}$  to react exactly with the  $\text{Cu}(\text{NO}_3)_2$  in  $43.88 \text{ mL}$  of a  $0.3842 \text{ M}$  solution of  $\text{Cu}(\text{NO}_3)_2$ ?
- $$2\text{Cu}(\text{NO}_3)_2 + 4\text{KI} \rightarrow 2\text{CuI} + \text{I}_2 + 4\text{KNO}_3$$
17. A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared

by the reaction of acetic acid with calcium hydroxide.  
 $2\text{CH}_3\text{CO}_2\text{H} + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{CH}_3\text{CO}_2)_2 + 2\text{H}_2\text{O}$   
 What mass of  $\text{Ca}(\text{OH})_2$  is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

18. The toxic pigment called white lead,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , has been replaced in white paints by rutile,  $\text{TiO}_2$ . How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite ( $\text{FeTiO}_3$ ) by mass?  
 $2\text{FeTiO}_3 + 4\text{HCl} + \text{Cl}_2 \rightarrow 2\text{FeCl}_3 + 2\text{TiO}_2 + 2\text{H}_2\text{O}$

Show Selected Answers

2. The moles and the mass for each reaction are as follows:

- 0.435 mol Na, 0.271 mol  $\text{Cl}_2$ , 15.4 g  $\text{Cl}_2$
- 0.005780 mol  $\text{HgO}$ ,  $2.890 \times 10^{-3}$  mol  $\text{O}_2$ ,  $9.248 \times 10^{-2}$  g  $\text{O}_2$
- 8.00 mol  $\text{NaNO}_3$ ,  $6.8 \times 10^2$  g  $\text{NaNO}_3$
- 1665 mol  $\text{CO}_2$ , 73.3 kg  $\text{CO}_2$
- 18.86 mol  $\text{CuO}$ , 2.330 kg  $\text{CuCO}_3$
- 0.4580 mol  $\text{C}_2\text{H}_4\text{Br}_2$ , 86.05 g  $\text{C}_2\text{H}_4\text{Br}_2$

4. The moles and the mass for each reaction are as follows:

- $$\text{mol Mg} = 5.00 \text{ g } \cancel{\text{HCl}} \times \frac{1 \text{ mol } \cancel{\text{HCl}}}{36.4606 \text{ g}} \times \frac{1 \text{ mol Mg}}{2 \text{ mol } \cancel{\text{HCl}}} = 0.0686 \text{ mol,}$$

$$\text{g Mg} = 0.0686 \text{ mol } \cancel{\text{Mg}} \times \frac{24.305 \text{ g}}{1 \text{ mol } \cancel{\text{Mg}}} = 1.67 \text{ g}$$
- $$\text{mol O}_2 = 1.252 \text{ g } \cancel{\text{Ag}_2\text{O}} \times \frac{1 \text{ mol } \cancel{\text{Ag}_2\text{O}}}{231.7358 \text{ g}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol } \cancel{\text{Ag}_2\text{O}}} = 2.701 \times 10^{-3}$$

$$\begin{aligned}
 & \text{g O}_2 = 2.701 \times 10^{-3} \cancel{\text{mol O}_2} \times \frac{31.9988 \text{ g}}{1 \cancel{\text{mol O}_2}} = 0.08644 \text{ g} \\
 \text{c. } & \text{mol MgCO}_3 = 283 \cancel{\text{g CO}_2} \times \frac{1 \cancel{\text{mol CO}_2}}{44.010 \cancel{\text{g}}} \times \frac{1 \text{ mol MgCO}_3}{1 \cancel{\text{mol CO}_2}} = 6.43 \text{ mol}, \\
 & \text{g MgCO}_3 = 6.43 \cancel{\text{mol MgCO}_3} \times \frac{84.314 \text{ g}}{1 \cancel{\text{mol MgCO}_3}} = 542 \text{ g} \\
 \text{d. } & \text{mol H}_2\text{O} = 2.00 \times 10^4 \cancel{\text{g C}_2\text{H}_4} \times \frac{1 \cancel{\text{mol C}_2\text{H}_2}}{28.054 \cancel{\text{g}}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \cancel{\text{mol C}_2\text{H}_2}} = 713 \text{ mol}, \\
 & \text{g H}_2\text{O} = 713 \cancel{\text{mol H}_2\text{O}} \times \frac{18.01528 \cancel{\text{g}}}{1 \cancel{\text{mol H}_2\text{O}}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} = 12.8 \text{ kg} \\
 \text{e. } & 2.500 \cancel{\text{kg BaO}} \times \frac{1000 \cancel{\text{g BaO}}}{1 \cancel{\text{kg BaO}}} \times \frac{1 \cancel{\text{mol BaO}}}{153.326 \cancel{\text{g BaO}}} \times \frac{2 \text{ mol BaO}_2}{2 \cancel{\text{mol BaO}}} = 16.31 \text{ mol BaO}_2 \\
 & 16.31 \cancel{\text{mol BaO}_2} \times \frac{169.326 \text{ g BaO}_2}{1 \cancel{\text{mol BaO}_2}} = 2762 \text{ g BaO}_2 \\
 \text{f. } & 9.55 \cancel{\text{g C}_2\text{H}_6\text{O}} \times \frac{1 \cancel{\text{mol C}_2\text{H}_6\text{O}}}{46.068 \cancel{\text{g C}_2\text{H}_6\text{O}}} \times \frac{1 \text{ mol C}_2\text{H}_4}{1 \cancel{\text{mol C}_2\text{H}_6\text{O}}} = 0.207 \text{ mol C}_2\text{H}_4 \\
 & 0.207 \cancel{\text{mol C}_2\text{H}_4} \times \frac{28.053 \cancel{\text{g C}_2\text{H}_4}}{1 \cancel{\text{mol C}_2\text{H}_4}} = 5.81 \text{ g C}_2\text{H}_4
 \end{aligned}$$

6. The answers are as follows:

$$\begin{aligned}
 \text{a. } & \text{volume HCl solution} \rightarrow \text{mol HCl} \rightarrow \text{mol GaCl}_3 \\
 \text{b. } & 2.6 \cancel{\text{L HCl}} \times \frac{1.44 \cancel{\text{mol HCl}}}{1 \cancel{\text{L HCl}}} \times \frac{2 \cancel{\text{mol GaCl}_3}}{6 \cancel{\text{mol HCl}}} \times \frac{180.079 \text{ g GaCl}_3}{1 \cancel{\text{mol GaCl}_3}} = 2.3 \times 10^2 \text{ g GaCl}_3
 \end{aligned}$$

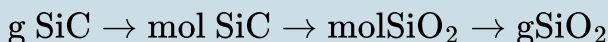
8. The development requires the following:

mass K [Ag(CN)<sub>2</sub>] → mol K [Ag(CN)<sub>2</sub>] → mol Zn(CN)<sub>2</sub> → molecules of Zn(CN)<sub>2</sub> g Zn(CN)<sub>2</sub>;

$$\begin{aligned}
 \text{a. } & 35.27 \text{ g K [Ag(CN)}_2] \times \frac{1 \cancel{\text{mol K [Ag(CN)}_2]}}{199.002 \cancel{\text{g K [Ag(CN)}_2]}} \times \frac{1 \cancel{\text{mol Zn(CN)}_2}}{2 \cancel{\text{mol K [Ag(CN)}_2]}} \times \frac{6.022 \times 10^{23}}{1 \cancel{\text{mol Zn(CN)}_2}} = 5.337 \times 10^{22} \text{ molecules} \\
 \text{b. } & 5.337 \times 10^{22} \cancel{\text{molecules}} \times \frac{1 \cancel{\text{mol Zn(CN)}_2}}{6.022 \times 10^{23} \cancel{\text{molecules}}} \times \frac{117.43 \text{ g Zn(CN)}_2}{1 \cancel{\text{mol Zn(CN)}_2}} = 10.41 \text{ g Zn(CN)}_2
 \end{aligned}$$

10.  $\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$ . From the balanced equation, 1 mol of SiO<sub>2</sub> produces 1 mol of SiC. The unknown is the mass of SiO<sub>2</sub> required to produce 3.00 kg (3000 g) of SiC. To calculate the mass of SiO<sub>2</sub> required,

determine the molar masses of  $\text{SiO}_2$  and  $\text{SiC}$ . Then calculate the number of moles of  $\text{SiC}$  required, and through the mole relation of  $\text{SiO}_2$  to  $\text{SiC}$ , find the mass of  $\text{SiO}_2$  required. The conversions required are:



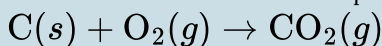
Molar masses:  $\text{SiO}_2 = 60.0843 \text{ g mol}^{-1}$ ;  $\text{SiC} = 40.0955 \text{ g mol}^{-1}$

$$\text{mass SiO}_2 = 3000 \text{ g SiC} \times \frac{1 \text{ mol SiC}}{40.955 \text{ g SiC}} \times \frac{1 \text{ mol SiO}_2}{1 \text{ mol SiC}} \times \frac{60.843 \text{ g SiO}_2}{1 \text{ mol SiO}_2} = 4496 \text{ g SiO}_2 = 4.50 \text{ kg SiO}_2$$

$$12. \text{ Molar mass urea} = 12.011 + 15.9994 + 2(14.0067) + 4(1.0079) = 60.054 \text{ g mol}^{-1}$$

$$\begin{aligned} 1 \text{ mol C} &\rightarrow 1 \text{ mol CO}_2 \rightarrow 1 \text{ mol urea} \\ \text{mass urea} &= 1.00 \times 10^3 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \frac{1 \text{ mol urea}}{1 \text{ mol C}} \times \frac{60.054 \text{ g urea}}{1 \text{ mol urea}} \\ &= 5.00 \times 10^6 \text{ g or } 5.00 \times 10^3 \text{ kg} \end{aligned}$$

14. The balanced chemical equation is



$$\begin{aligned} 500 \text{ miles} &\times \frac{1 \text{ gallon}}{37.5 \text{ miles}} \times \frac{3.785 \text{ L}}{1 \text{ gallon}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.8205 \text{ g gas}}{1 \text{ mL gas}} \times \frac{84.2 \text{ g C}}{100 \text{ g gas}} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \\ &\times \frac{1 \text{ mol O}_2}{1 \text{ mol C}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} = 1.28 \times 10^5 \text{ g CO}_2 \end{aligned}$$

16. Use molarity to convert. This solution involves the following steps:

- Converting the volume of KI to moles of KI
- Converting the moles of KI to moles of  $\text{Cu}(\text{NO}_3)_2$
- Converting the moles of  $\text{K} \rightarrow \text{Cu}(\text{NO}_3)_2$  to a volume of  $\text{KI}$ .  $\text{Cu}(\text{NO}_3)_2$  solution

$$43.88 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.3842 \text{ mol Cu}(\text{NO}_3)_2}{1 \text{ L}} \times \frac{4 \text{ mol KI}}{2 \text{ mol Cu}(\text{NO}_3)_2} \times \frac{1 \text{ L KI}}{0.2089 \text{ mol KI}} = 161.4 \text{ mL}$$

All of these steps can be shown together, as follows:

$$\frac{43.88 \text{ mL Cu}(\text{NO}_3)_2}{1} \times \frac{0.3842 \text{ mol Cu}(\text{NO}_3)_2}{1000 \text{ mL Cu}(\text{NO}_3)_2} \times \frac{4 \text{ mol KI}}{2 \text{ mol Cu}(\text{NO}_3)_2} \times \frac{1000 \text{ mL KI}}{0.2089 \text{ mol KI}} = 161.40 \text{ mL KI solution}$$

18. Find from worked example, check your learning problem

$$\text{mass of ilmenite} = 379 \cancel{\text{ g ore}} \times \frac{0.883 \text{ gFeTiO}_3}{1 \cancel{\text{ g ore}}} = 334.6 \text{ gFeTiO}_3$$

$$\text{mass of rutile} = 334.6 \cancel{\text{ gFeTiO}_3} \times \frac{1 \cancel{\text{ molFeTiO}_3}}{151.7 \cancel{\text{ gFeTiO}_3}} \times \frac{2 \cancel{\text{ molTiO}_2}}{2 \cancel{\text{ molFeTiO}_3}} \times \frac{79.88 \text{ gTiO}_2}{1 \cancel{\text{ molTiO}_2}} = 176 \text{ gTiO}_2$$

## Glossary

**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



PART X  
GASES





## 39. 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 1). 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.

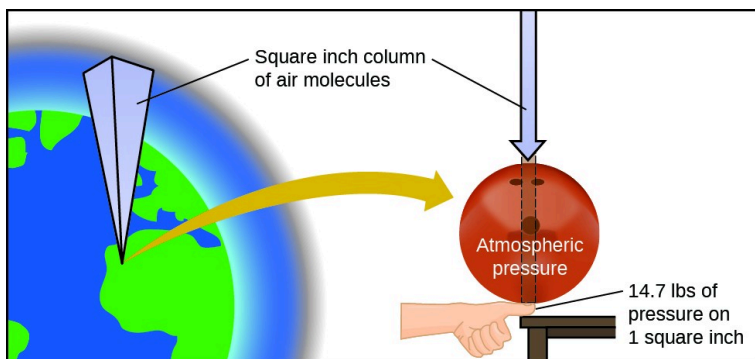


Figure 1. The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.



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<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=64#oembed-1>

A smaller scale demonstration of this phenomenon is briefly explained in the following video:



One or more interactive elements has been excluded from this version of the text. You can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=64#oembed-2>

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 2—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  $250 \text{ in}^2$ ), so the pressure exerted by each foot is about  $14 \text{ lb/in}^2$ :

$$\text{pressure per elephant foot} = 14,000 \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about  $2 \text{ in}^2$ , so the pressure exerted by each blade is about  $30 \text{ lb/in}^2$ :

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2$$

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 2. 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; credit b: modification of work by Ryosuke Yagi)

The SI unit of pressure is the **pascal (Pa)**, with  $1 \text{ Pa} = 1 \text{ N/m}^2$ , where N is the newton, a unit of force defined as  $1 \text{ kg m/s}^2$ . One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal ( $1 \text{ kPa} = 1000 \text{ Pa}$ ) or **bar** ( $1 \text{ bar} = 100,000 \text{ Pa}$ ). 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 1 provides some information on these and a few other common units for pressure measurements

Table 1. Pressure Units	
Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	1 Pa = 1 N/m <sup>2</sup> 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

*Example 1: 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:

1. torr
2. atm
3. kPa
4. mbar

Show Answer

This is a unit conversion problem. The relationships between the various pressure units are given in Table 1.

$$1. \quad 29.2 \cancel{\text{ in Hg}} \times \frac{760 \text{ torr}}{29.92 \cancel{\text{ in Hg}}} = 742 \text{ torr}$$

$$2. \quad 742 \cancel{\text{ torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{ torr}}} = 0.976 \text{ atm}$$

$$3. \quad 742 \cancel{\text{ torr}} \times \frac{101.325 \text{ kPa}}{760 \cancel{\text{ torr}}} = 98.9 \text{ kPa}$$

$$4. \quad 98.9 \cancel{\text{ kPa}} \times \frac{1000 \cancel{\text{ Pa}}}{1 \cancel{\text{ kPa}}} \times \frac{1 \cancel{\text{ bar}}}{100,000 \cancel{\text{ Pa}}} \times \frac{1000 \text{ mbar}}{1 \cancel{\text{ bar}}} = 989 \text{ mbar}$$

### Check Your Learning

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Show Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a barometer (Figure 3). 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.

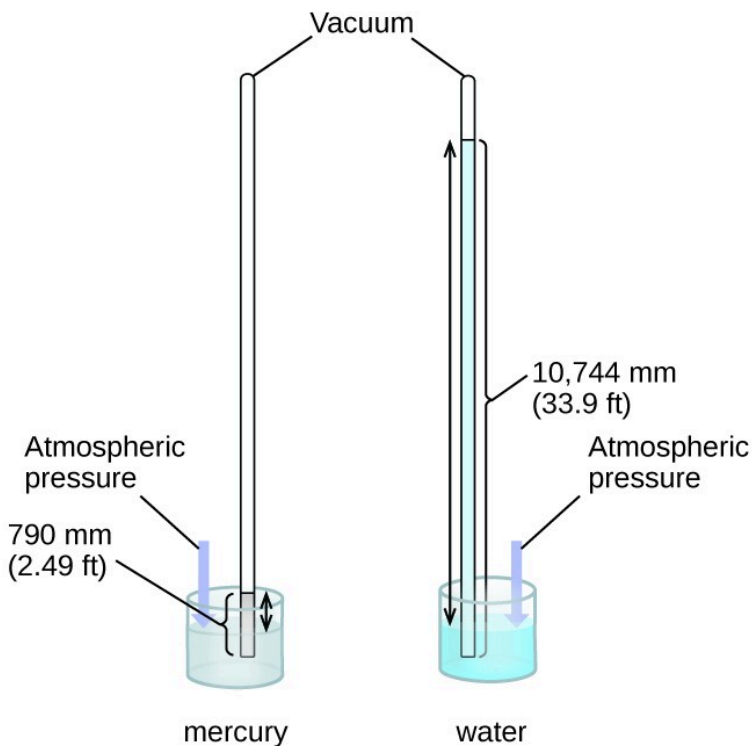


Figure 3. In a barometer, the height,  $h$ , of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

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 millimeter 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,  $\rho$  is the density of the fluid, and  $g$  is acceleration due to gravity.

### *Example 2: 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<sup>3</sup>.

Show Answer

The hydrostatic pressure is given by  $p = h\rho g$ , with  $h = 760$  mm,  $\rho = 13.6$  g/cm<sup>3</sup>, and  $g = 9.81$  m/s<sup>2</sup>. 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.)

$$\begin{aligned} 101,325 \text{ N/m}^2 &= 101,325 \frac{\text{kg} \cdot \text{m/s}^2}{\text{m}^2} = 101,325 \frac{\text{kg}}{\text{m} \cdot \text{s}^2} \\ p &= \left( 760 \text{ mm} \times \frac{1 \text{ m}}{1000 \text{ mm}} \right) \times \left( \frac{13.6 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{(100 \text{ cm})^3}{(1 \text{ m})^3} \right) \times \left( \frac{9.81 \text{ m}}{1 \text{ s}^2} \right) \\ &= (0.760 \text{ m}) (13,600 \text{ kg/m}^3) (9.81 \text{ m/s}^2) = 1.01 \times 10^5 \text{ kg/ms}^2 = 1.01 \times 10^5 \text{ N/m}^2 \\ &= 1.01 \times 10^5 \text{ Pa} \end{aligned}$$



## Check Your Learning

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<sup>3</sup>.

Show Answer

10.3 m

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 4) 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.

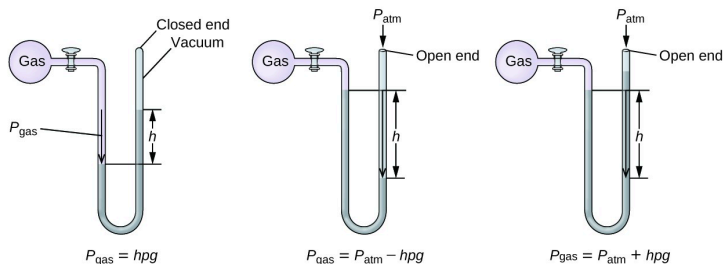
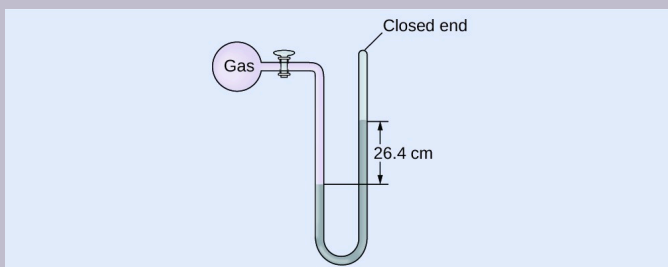


Figure 4. A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels ( $h$ ) is a measure of the pressure. Mercury is usually used because of its large density.

### Example 3: Calculation of Pressure Using a Closed-End Manometer

The pressure of a sample of gas is measured with a closed-end manometer, as shown below.



The liquid in the manometer is mercury. Determine the pressure of the gas in:

1. torr
2. Pa
3. bar

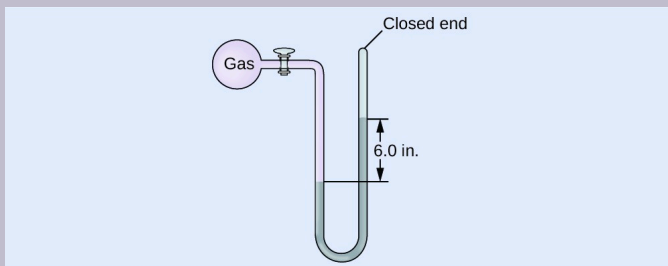
Show Answer

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 2, but it is simpler to just convert between units using Table 1.

1.  $26.4 \cancel{\text{ cm Hg}} \times \frac{10 \cancel{\text{ mm Hg}}}{1 \cancel{\text{ cm Hg}}} \times \frac{1 \text{ torr}}{1 \cancel{\text{ mm Hg}}} = 264 \text{ torr}$
2.  $264 \cancel{\text{ torr}} \times \frac{1 \cancel{\text{ atm}}}{760 \cancel{\text{ torr}}} \times \frac{101,325 \text{ Pa}}{1 \cancel{\text{ atm}}} = 35,200 \text{ Pa}$
3.  $35,200 \cancel{\text{ Pa}} \times \frac{1 \text{ bar}}{100,000 \cancel{\text{ Pa}}} = 0.352 \text{ bar}$

### Check Your Learning

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:

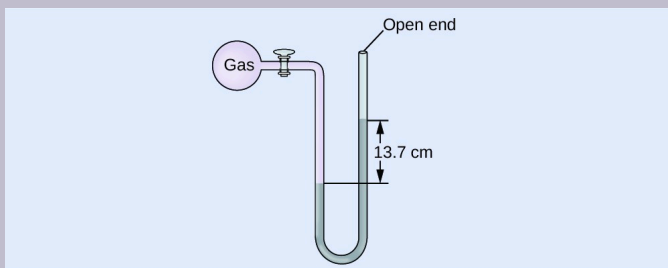
1. torr
2. Pa
3. bar

Show Answer

1. ~150 torr
2. ~20,000 Pa
3. ~0.20 bar

### *Example 4: 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 below.



Determine the pressure of the gas in:

1. mm Hg
2. atm
3. kPa

Show Answer

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.)

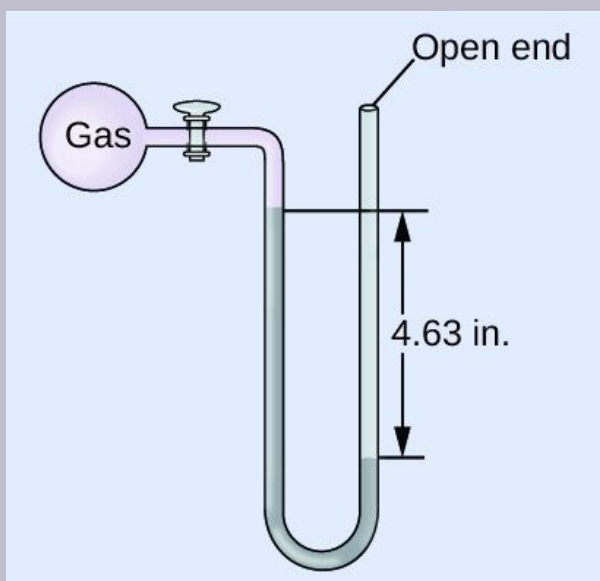
$$1. \quad \text{In mm Hg, this is: } 137 \text{ mm Hg} + 760 \text{ mm Hg} = 897 \text{ mm Hg}$$

$$2. \quad \cancel{897 \text{ mm Hg}} \times \frac{1 \text{ atm}}{\cancel{760 \text{ mm Hg}}} = 1.18 \text{ atm}$$

$$3. \quad \cancel{1.18 \text{ atm}} \times \frac{101.325 \text{ kPa}}{\cancel{1 \text{ atm}}} = 1.20 \times 10^2 \text{ kPa}$$

### *Check Your Learning*

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown below.



Determine the pressure of the gas in:

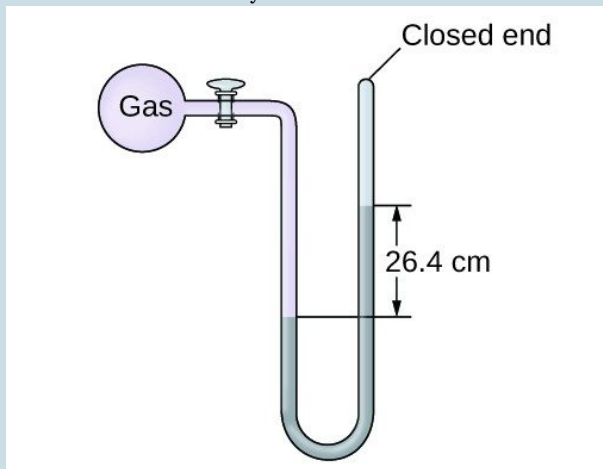
1. mm Hg
2. atm
3. kPa

Show Answer

1. 642 mm Hg
2. 0.845 atm
3. 85.6 kPa

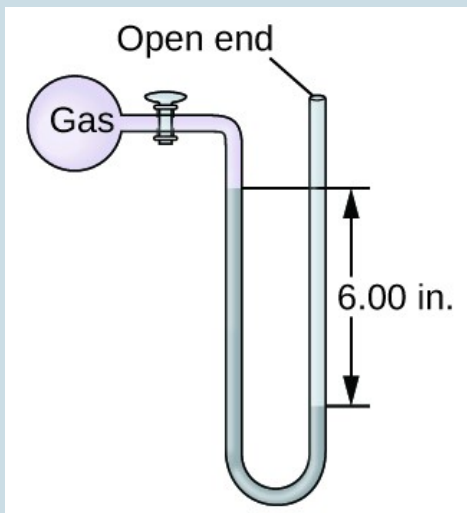
## Exercises

1. The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury.



Determine the pressure of the gas in:

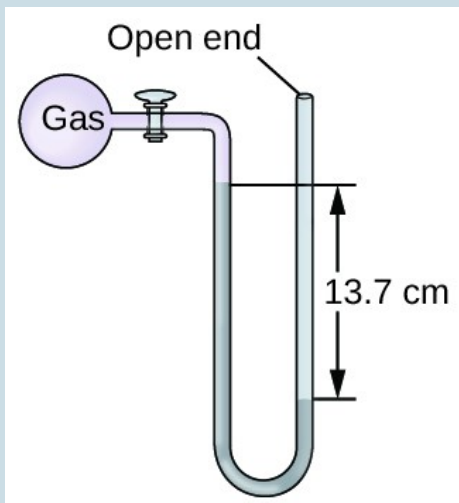
- a. torr
  - b. Pa
  - c. bar
2. The pressure of a sample of gas is measured with an open-end manometer, partially shown to the right. The liquid in the manometer is mercury.



Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:

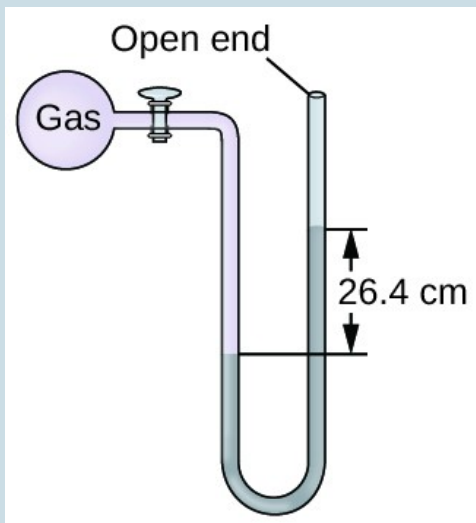
- a. torr
  - b. Pa
  - c. bar
3. The pressure of a sample of gas is measured at sea level with an open-end mercury manometer.





Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:

- a.    mm Hg
  - b.    atm
  - c.    kPa
4.    The pressure of a sample of gas is measured at sea level with an open-end mercury manometer.



Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:

- a. mm Hg
- b. atm
- c. kPa

Show Selected Answer

1. The pressure of the gas is:

- a.  $26.4 \cancel{\text{ cm}} \times \frac{10 \cancel{\text{ mm}}}{1 \cancel{\text{ cm}}} \times \frac{1 \text{ torr}}{1 \cancel{\text{ mm}}} = 264 \text{ torr}$
- b.  $264 \text{ torr} \times \frac{101,325 \text{ Pa}}{760 \text{ torr}} = 35,200 \text{ Pa}$
- c.  $264 \cancel{\text{ torr}} \times \frac{1.01325 \text{ bar}}{760 \cancel{\text{ torr}}} = 0.352 \text{ bar}$

3. The pressure of the gas equals the hydrostatic pressure due to the pressure of the atmosphere at sea level minus a

column of mercury of height 13.7 cm. The pressure on the left is due to the gas and the pressure on the right is due to the atmospheric pressure minus 13.7 cm Hg).

a. In mm Hg, this is:  $760 \text{ mm Hg} - 137 \text{ mm Hg} = 623 \text{ mm Hg}$ ;

b. 
$$623 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.820 \text{ atm};$$

c. 
$$0.820 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 83.1 \text{ kPa}$$

## 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 5). 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 millimeters of mercury (mm Hg).



(a)



(b)

Figure 5. (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: modification of work by Master Sgt. Jeffrey Allen)

## 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 (Figure 6) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

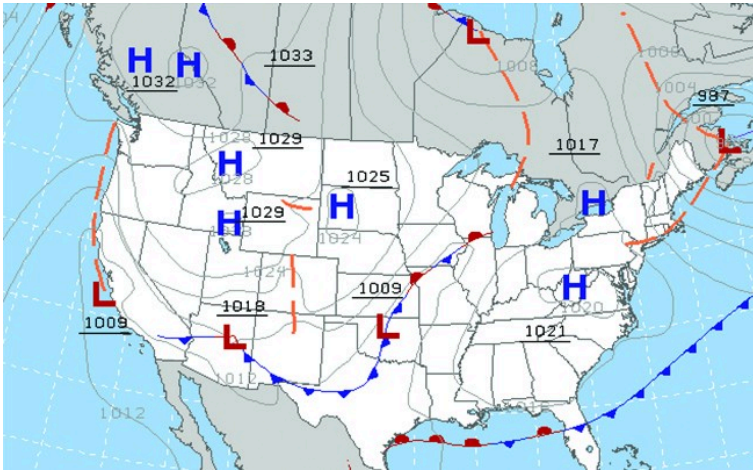


Figure 6. Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

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 7: 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.

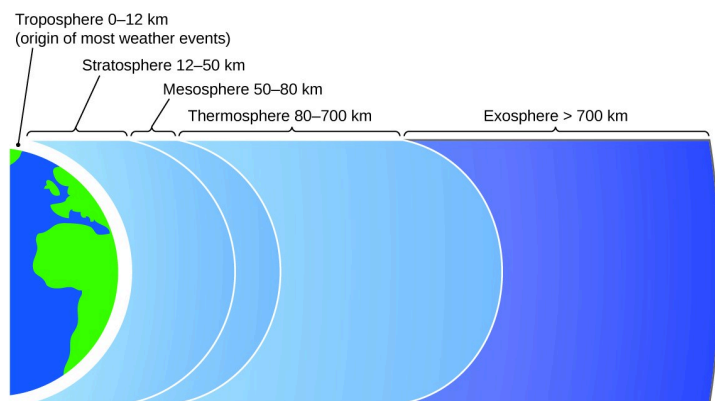


Figure 7. Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

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.

## *Key Concepts and Summary*

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.

### *Key Equations*

- $P = \frac{F}{A}$
- $p = h\rho g$

### *Exercises*

1. Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?
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?
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?
6. A typical barometric pressure in Kansas City is 740

- torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?
- Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?
  - 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?
  - 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.
  - 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?
  - 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.
    - What was the pressure in kPa?
    - 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.
  - Why is it necessary to use a nonvolatile liquid in a barometer or manometer?
  - How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers



vs. closed-end manometers?

### Selected Answers

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.

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.

5. Convert 615 mm Hg to atmospheres using 760 mm Hg = 1 atm. Use 1 atm = 101.325 kPa in the second part

$$615 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.809 \text{ atm}$$
$$0.809 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 82.0 \text{ kPa}$$

7.

$$32.0 \cancel{\text{ lb}} \cancel{\text{ in}^{-2}} \times \frac{1 \cancel{\text{ atm}}}{14.7 \cancel{\text{ lb}} \cancel{\text{ in}^{-2}}} \times \frac{101.325 \text{ kPa}}{1 \cancel{\text{ atm}}} = 2.2 \times 10^2 \text{ kPa}$$

9. Identify:  $14.7 \text{ lb in}^{-2} = 1 \text{ atm}$

$$88.8 \cancel{\text{ atm}} \times \frac{14.7 \text{ lb in}^{-2}}{1 \cancel{\text{ atm}}} = 13.1 \times 10^3 \text{ lb in}^{-2}$$

11. The answers are as follows:

$$1. \quad 29.97 \cancel{\text{ in Hg}} \times \frac{101.325 \text{ kPa}}{29.92 \cancel{\text{ in Hg}}} = 101.5 \text{ kPa}$$

$$2. \quad 28.0 \text{ in. } \cancel{\text{Hg}} \times \frac{760 \text{ torr}}{29.92 \text{ in. } \cancel{\text{Hg}}} = 711 \text{ torr};$$

$$762 - 711 = 51 \text{ torr drop}$$

13. 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  $P_{\text{gas}} = P_{\text{atm}} + P_{\text{vol liquid}}$ .

## Glossary

**atmosphere (atm):** unit of pressure; 1 atm = 101,325 Pa

**bar:** (bar or b) unit of pressure; 1 bar = 100,000 Pa

**barometer:** device used to measure atmospheric pressure

**hydrostatic pressure:** pressure exerted by a fluid due to gravity

**manometer:** device used to measure the pressure of a gas trapped in a container

**pascal (Pa):** SI unit of pressure; 1 Pa = 1 N/m<sup>2</sup> **pounds per square**

**inch (psi):** unit of pressure common in the US

**pressure:** force exerted per unit area

**torr:** unit of pressure;  $1 \text{ torr} = \frac{1}{760} \text{ atm}$

# 40. 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 1), 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.

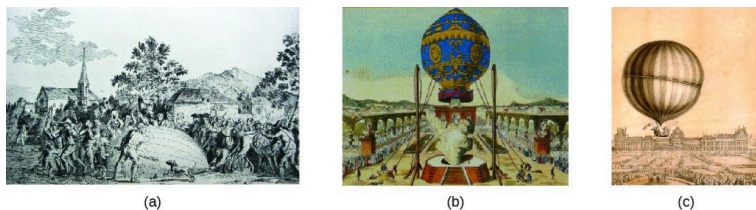


Figure 1. In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

## Pressure and Temperature: Amontons'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 2) and the pressure increases.

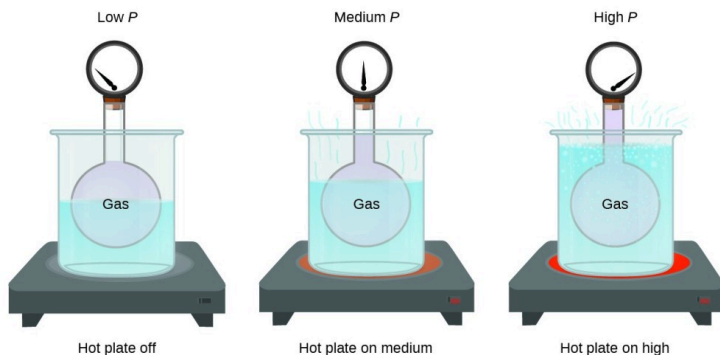


Figure 2. The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

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 3. 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.

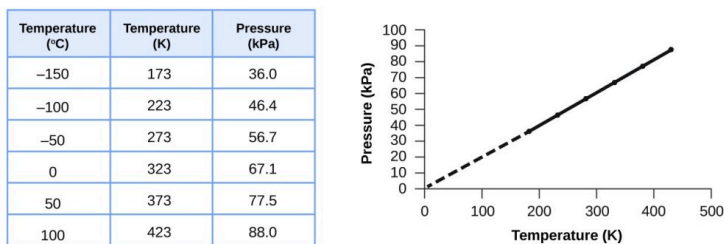


Figure 3. For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at  $-273^{\circ}\text{C}$ , which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

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's 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  $\propto$  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 1: Predicting Change in Pressure with Temperature*

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

1. On the can is the warning “Store only at temperatures below 120 °F (48.8 °C). Do not incinerate.” Why?
2. 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?

Show Answer

1. 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.)
2. We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/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:

$$P_2 = \frac{360 \text{ kPa} \times 323 \cancel{\text{K}}}{297 \cancel{\text{K}}} = 390 \text{ kPa}$$

### *Check Your Learning*

A sample of nitrogen,  $\text{N}_2$ , 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?

Show Answer

400 torr

## 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.

This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.





One or more interactive elements has been excluded from this version of the text. You

can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=65#oembed-1>

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 Figure 4.

Temperature (°C)	Temperature (K)	Volume (L)
-3	270	22
-23	250	21
-53	220	18
-162	111	9

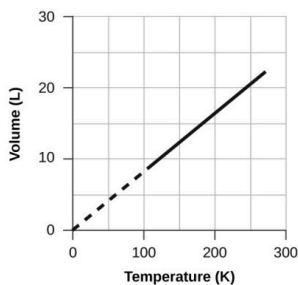


Figure 4. The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given

amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's 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 V-T relationship, this leads to another form of Charles's law:  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ .

### *Example 2: Predicting Change in Volume with Temperature*

A sample of carbon dioxide,  $\text{CO}_2$ , occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Show Answer

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:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{ which means that } \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

Rearranging and solving gives:

$$V_2 = \frac{0.300\text{L} \times 303\cancel{\text{K}}}{283\cancel{\text{K}}} = 0.321\text{ L}$$

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).

### *Check Your Learning*

A sample of oxygen, O<sub>2</sub>, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at -70 °C and the same pressure?

Show Answer

21.6 mL

### *Example 3: 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<sup>3</sup> 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

$\text{cm}^3$ . Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Show Answer

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  $^{\circ}\text{C}$  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

$$T_2 = \frac{131.7 \cancel{\text{cm}^3} \times 273.15 \text{ K}}{150.0 \cancel{\text{cm}^3}} = 239.8 \text{ K}$$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is  $-33.4^{\circ}\text{C}$ .

### *Check Your Learning*

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?

Show Answer

635 mL

## 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 5.

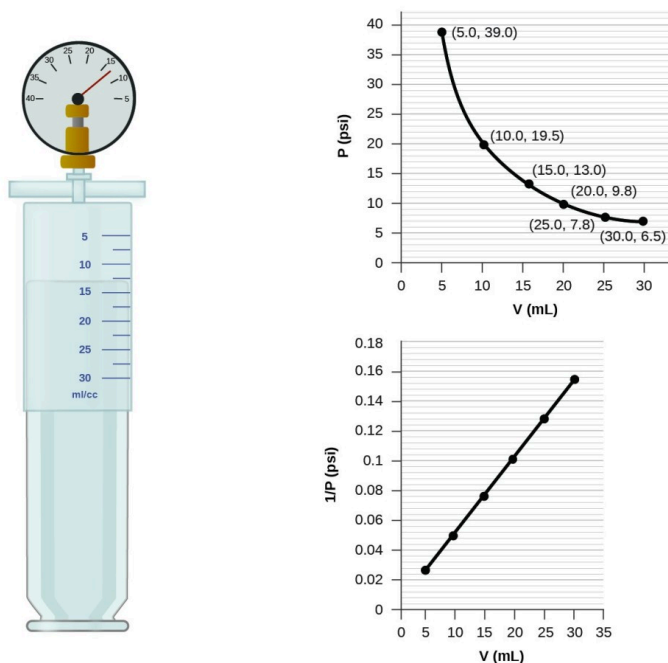


Figure 5. When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since  $P$  and  $V$  are inversely proportional, a graph of  $1/P$  vs.  $V$  is linear.

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:

$$P \propto 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1 V_1 = P_2 V_2$$

with  $k$  being a constant.

Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure

$\left(\frac{1}{P}\right)$  versus the volume ( $V$ ), or the inverse of volume  $\left(\frac{1}{V}\right)$  versus the pressure

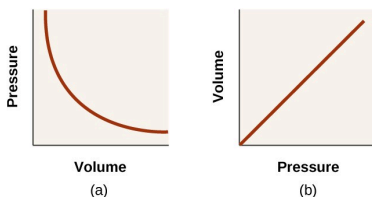


Figure 6. The relationship between pressure and volume is inversely proportional. (a) The graph of  $P$  vs.  $V$  is a parabola, whereas (b) the graph of  $(1/P)$  vs.  $V$  is linear.

( $V$ ). 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 6).

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 4: Volume of a Gas Sample

The sample of gas in Figure 5 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:

1. the P-V graph in Figure 5
2. the  $\frac{1}{P}$  vs. V graph in Figure 5
3. the Boyle's law equation

Comment on the likely accuracy of each method.

Show Answer

1. Estimating from the P-V graph gives a value for P somewhere around 27 psi.
2. Estimating from the  $\frac{1}{P}$  versus V graph give a value of about 26 psi.
3. 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 0.993 atm and 2.40 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:

$$V_2 = \frac{13.0 \text{ psi} \times 15.0 \cancel{\text{ mL}}}{7.5 \cancel{\text{ mL}}} = 26 \text{ mL}$$

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.

### *Check Your Learning*

The sample of gas in Figure 5 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 mL, using:

1. the P-V graph in Figure 5
2. the  $\frac{1}{P}$  vs. V graph in Figure 5
3. the Boyle's law equation

Comment on the likely accuracy of each method.

Show Answer

1. about 17–18 mL
2. ~18 mL
3. 17.7 mL

It was more difficult to estimate well from the P-V graph, so (1) is likely more inaccurate than (2); the calculation will be as accurate as the equation and measurements allow.

## Chemistry in Action: 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 7).

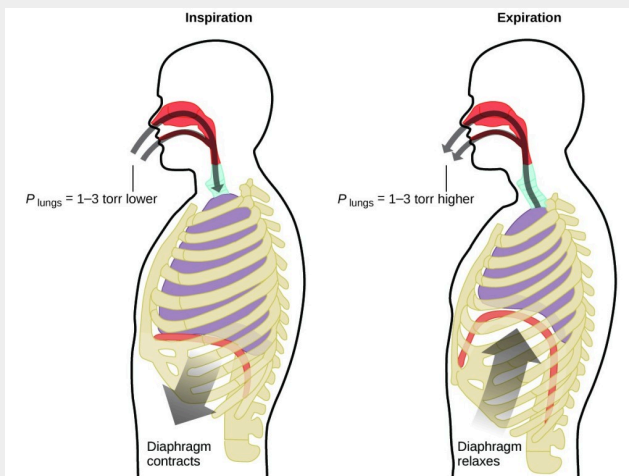


Figure 7. Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

## Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior 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:

$$V \propto n \quad \text{or} \quad V = k \times n \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as  $P$  versus  $n$ , and  $n$  versus  $T$ .

Visit this interactive [PhET simulation link to investigate the relationships between pressure, volume, temperature, and amount of gas](#). Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

## 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:  $PV = \text{constant}$  at constant  $T$  and  $n$
- Amontons's law:  $\frac{P}{T} = \text{constant}$  at constant  $V$  and  $n$
- Charles's law:  $\frac{V}{T} = \text{constant}$  at constant  $P$  and  $n$
- Avogadro's law:  $\frac{V}{n} = \text{constant}$  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  $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$  and  $8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1}$ .

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 behavior* 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 behavior, 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* behavior 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 5: Using the Ideal Gas Law*

Methane,  $\text{CH}_4$ , is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of  $\text{CH}_4$ . What is the volume of this much methane at  $25^\circ\text{C}$  and 745 torr?

Show Answer

We must rearrange  $PV = nRT$  to solve for  $V$ :

$$V = \frac{nRT}{P}$$

If we choose to use  $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ , then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the “right” units:

$$n = 655 \text{ g } \cancel{\text{CH}_4} \times \frac{1 \text{ mol}}{16.043 \text{ g } \cancel{\text{CH}_4}} = 40.8 \text{ mol}$$

$$T = 25^\circ \text{ C} + 273 = 298 \text{ K}$$

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \text{ mol}) (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (298 \text{ K})}{0.980 \text{ atm}} = 1.02 \times 10^3 \text{ L}$$

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.

### *Check Your Learning*

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at  $27^\circ \text{ C}$  in the 180-L storage tank of a modern hydrogen-powered car.

Show Answer

350 bar

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:  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  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 constant).

### Example 6: 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 8). If the water temperature is 27 °C, how many liters 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 8. Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Show Answer

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:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow \frac{(153 \text{ atm})(13.2 \text{ L})}{(300 \text{ K})} = \frac{(3.13 \text{ atm})(V_2)}{(310 \text{ K})}$$

Solving for  $V_2$ :

$$V_2 = \frac{(153 \text{ atm}) (13.2 \text{ L}) (310 \text{ K})}{(300 \text{ K}) (3.13 \text{ atm})} = 667 \text{ L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior 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.)

### *Check Your Learning*

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.

Show Answer

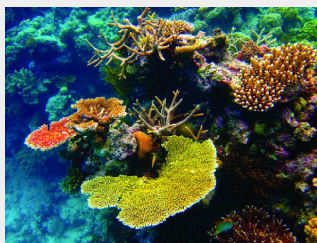
0.538 L

## The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 9) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.

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



*Figure 9. 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: Kyle Taylor)*



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.

## 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 10).

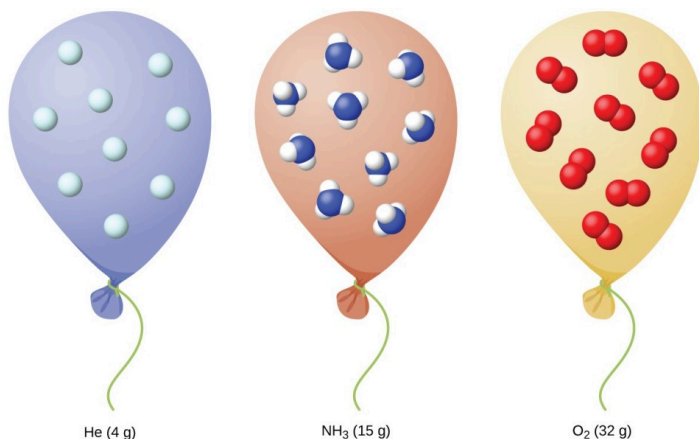


Figure 10. Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

### *Key Concepts and Summary*

The behavior 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 (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's 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.

### *Key Equations*

- $PV = nRT$

### *Exercises*

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 8) change as they rise to the

- surface, assuming that they remain intact.
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?
  5. How would the graph in Figure 4 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 5 change if the number of moles of gas in the sample used to determine the curve were doubled?
  7. In addition to the data found in Figure 5, 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  $\text{CH}_4$  gas at 150 K and 1 atm, using Figure 4.
  9. Determine the pressure of the gas in the syringe shown in Figure 5 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 ( $T = 475\text{ }^{\circ}\text{C}$ ), what will be the pressure in the hot can?
  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  $-196\text{ }^{\circ}\text{C}$  is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.
  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?
  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,  $\text{BF}_3$ , are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of  $\text{BF}_3$ ?
  17. Iodine,  $\text{I}_2$ , is a solid at room temperature but sublimates (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  $\text{I}_2$  vapor 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  $\text{CO}_2$  at 307 torr and  $26^\circ\text{C}$
  - b. 8.75 L of  $\text{C}_2\text{H}_4$ , at 378.3 kPa and 483 K
  - c. 221 mL of Ar at 0.23 torr and  $-54^\circ\text{C}$
19. A high altitude balloon is filled with  $1.41 \times 10^4$  L of hydrogen at a temperature of  $21^\circ\text{C}$  and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is  $-48^\circ\text{C}$  and the pressure is 63.1 torr?
20. A cylinder of medical oxygen has a volume of 35.4 L, and contains  $\text{O}_2$  at a pressure of 151 atm and a temperature of  $25^\circ\text{C}$ . What volume of  $\text{O}_2$  does this correspond to at normal body conditions, that is, 1 atm and  $37^\circ\text{C}$ ?
21. A large scuba tank (Figure 8) with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at  $20^\circ\text{C}$  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  $20^\circ\text{C}$ ?
22. A 20.0-L cylinder containing 11.34 kg of butane,  $\text{C}_4\text{H}_{10}$ , 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  $27^\circ\text{C}$ .
23. While resting, the average 70-kg human male consumes 14 L of pure  $\text{O}_2$  per hour at  $25^\circ\text{C}$  and 100 kPa. How many moles of  $\text{O}_2$  are consumed by a 70 kg man while resting for 1.0 h?

24. For a given amount of gas showing ideal behavior, draw labeled graphs of:
- the variation of  $P$  with  $V$
  - the variation of  $V$  with  $T$
  - the variation of  $P$  with  $T$
  - the variation of  $\frac{1}{P}$  with  $V$
25. A liter of methane gas,  $\text{CH}_4$ , at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas,  $\text{H}_2$ , at STP. Using Avogadro's law as a starting point, explain why.
26. The effect of chlorofluorocarbons (such as  $\text{CCl}_2\text{F}_2$ ) on the depletion of the ozone layer is well known. The use of substitutes, such as  $\text{CH}_3\text{CH}_2\text{F}(g)$ , for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:
- $\text{CCl}_2\text{F}_2(g)$
  - $\text{CH}_3\text{CH}_2\text{F}(g)$
27. As 1 g of the radioactive element radium decays over 1 year, it produces  $1.16 \times 10^{18}$  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  $25^\circ\text{C}$ ?
28. A balloon that is 100.21 L at  $21^\circ\text{C}$  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  $5.24^\circ\text{C}$ ,

what is the pressure experienced by the balloon as it clears Mount Crumpet?

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?

#### Selected Answers

2. As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.
4. The answers are as follows:
  - a. The number of particles in the gas increases as the volume increases. This relationship may be written as  $n = \text{constant} \times V$ . It is a direct relationship.
  - b. The temperature and pressure must be kept constant.
6. The curve would be farther to the right and higher up, but the same basic shape.
8. The figure shows the change of 1 mol of  $\text{CH}_4$  gas as a function of temperature. The graph shows that the volume is about 16.3 to 16.5 L.
10. The first thing to recognize about this problem is that the volume and moles of gas remain constant. Thus, we can use the combined gas law equation in the form:

$$\frac{P_2}{T_2} = \frac{P_1}{T_1}$$
$$P_2 = \frac{P_1 T_2}{T_1} = 1344 \text{ torr} \times \frac{475 + 273.15}{23 + 273.15} = 3.40 \times 10^3 \text{ torr}$$



12. Apply Charles's law to compute the volume of gas at the higher temperature:

- $V_1 = 2.50 \text{ L}$
- $T_1 = -193^\circ\text{C} = 77.15 \text{ K}$
- $V_2 = ?$
- $T_2 = 100^\circ\text{C} = 373.15 \text{ K}$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{2.50 \text{ L} \times 373.15 \cancel{\text{K}}}{77.15 \cancel{\text{K}}} = 12.1 \text{ L}$$

14.  $PV = nRT$

$$V = \frac{nRT}{P} = \frac{8.80 \cancel{\text{mol}} \times 0.08206 \text{ L atm mol}^{-1} \cancel{\text{K}}^{-1} \times 298.15 \cancel{\text{K}}}{0.992 \cancel{\text{atm}}} = 217 \text{ L}$$

16.

$$n = \frac{PV}{RT} = \frac{1.220 \cancel{\text{atm}} (4.3410 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \cancel{\text{K}}^{-1}) (788.0 \cancel{\text{K}})} = 0.08190 \text{ mol} = 8.190 \times 10^{-2} \text{ mol}$$

$$n \times \text{molar mass} = 8.190 \times 10^{-2} \cancel{\text{mol}} \times 67.8052 \text{ g mol}^{-1} = 5.553 \text{ g}$$

18. In each of these problems, we are given a volume, pressure, and temperature. We can obtain moles from this information using the molar mass,  $m = n\mathcal{M}$ , where  $\mathcal{M}$  is the molar mass:

$$P, V, T \xrightarrow{n = PV/RT} n, \xrightarrow{m = n(\text{molar mass})} \text{grams}$$

or we can combine these equations to obtain:

$$\text{mass} = m = \frac{PV}{RT} \times \mathcal{M}$$

$$\text{a. } 307 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 0.4039 \text{ atm } 25^\circ \text{ C} = 299.1 \text{ K}$$

$$\text{Mass} = m = \frac{0.4039 \cancel{\text{atm}} (0.100 \cancel{\text{L}})}{0.08206 \cancel{\text{L}} \cancel{\text{atm}} \text{ mol}^{-1} \cancel{\text{K}}^{-1} (299.1 \cancel{\text{K}})} \times 44.01 \text{ g mol}^{-1} = 7.24 \times 10^{-2} \text{ g}$$

$$\text{b. } \text{Mass} = m = \frac{378.3 \cancel{\text{kPa}} (8.75 \cancel{\text{L}})}{8.314 \cancel{\text{L}} \cancel{\text{kPa}} \text{ mol}^{-1} \cancel{\text{K}}^{-1} (483 \cancel{\text{K}})} \times 28.05376 \text{ g mol}^{-1} = 23.1 \text{ g}$$

$$221 \cancel{\text{mL}} \times \frac{1 \text{ L}}{1000 \cancel{\text{mL}}} = 0.221 \text{ L} - 54^\circ \text{ C} + 273.15 = 219.15 \text{ K}$$

$$\text{c. } 0.23 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 3.03 \times 10^{-4} \text{ atm}$$

$$\text{Mass} = m = \frac{3.03 \times 10^{-4} \cancel{\text{atm}} (0.221 \cancel{\text{L}})}{0.08206 \cancel{\text{L}} \cancel{\text{atm}} \text{ mol}^{-1} \cancel{\text{K}}^{-1} (219.15 \cancel{\text{K}})} \times 39.978 \text{ g mol}^{-1} = 1.5 \times 10^{-4} \text{ g}$$

$$20. \frac{P_2}{T_2} = \frac{P_1}{T_1}$$

$$T_2 = 49.5 + 273.15 = 322.65 \text{ K}$$

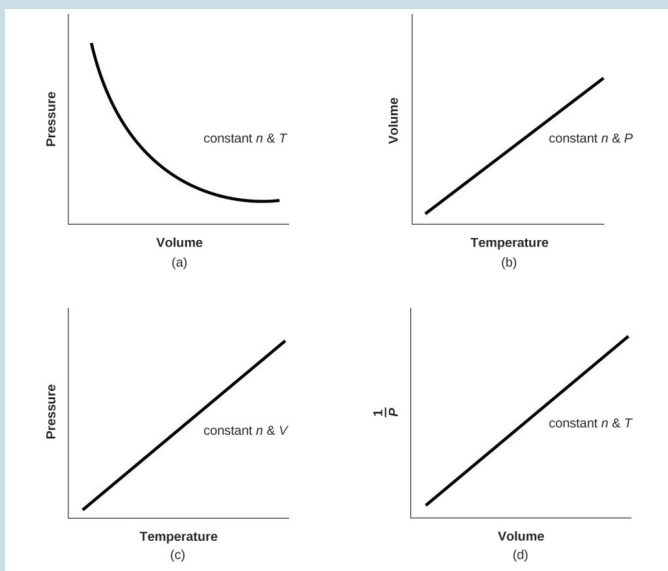
$$P_2 = \frac{P_1 T_2}{T_1} = 149.6 \text{ atm} \times \frac{322.65}{278.15} = 173.5 \text{ atm}$$

22. Calculate the amount of butane in 20.0 L at 0.983 atm and 27°C. The original amount in the container does not matter.

$$n = \frac{PV}{RT} = \frac{0.983 \cancel{\text{atm}} \times 20.0 \cancel{\text{L}}}{0.08206 \cancel{\text{L}} \cancel{\text{atm}} \text{ mol}^{-1} \cancel{\text{K}}^{-1} (300.1 \cancel{\text{K}})} = 0.798 \text{ mol}$$

$$\text{Mass of butane} = 0.798 \text{ mol} \times 58.1234 \text{ g/mol} = 46.4 \text{ g}$$

24. For a gas exhibiting ideal behavior:



26. The volume is as follows:

- a. Determine the molar mass of  $\text{CCl}_2\text{F}_2$  then calculate the moles of  $\text{CCl}_2\text{F}_2(g)$  present. Use the ideal gas law  $PV = nRT$  to calculate the volume of  $\text{CCl}_2\text{F}_2(g)$ :

$$10.0 \text{ g CCl}_2\text{F}_2 \times \frac{1 \text{ mol CCl}_2\text{F}_2}{120.91 \text{ g CCl}_2\text{F}_2} = 0.0827 \text{ mol CCl}_2\text{F}_2$$

$$PV = nRT, \text{ where } n = \# \text{ mol CCl}_2\text{F}_2$$

$$1 \text{ atm} \times V = 0.0827 \text{ mol} \times \frac{0.0821 \text{ L atm}}{\text{mol K}} \times 273 \text{ K} = 1.85 \text{ L CCl}_2\text{F}_2;$$

- b.  $10.0 \text{ g CH}_3\text{CH}_2\text{F} \times \frac{1 \text{ mol CH}_3\text{CH}_2\text{F}}{48.07 \text{ g CH}_3\text{CH}_2\text{F}} = 0.208 \text{ mol CH}_3\text{CH}_2\text{F}$

$$PV = nRT, \text{ with } n = \# \text{ mol CH}_3\text{CH}_2\text{F}$$

$$1 \text{ atm} \times V = 0.208 \text{ mol} \times 0.0821 \text{ L atm/mol K} \times 273 \text{ K} =$$

$$4.66 \text{ L CH}_3\text{CH}_2\text{F}$$

28. Identify the variables in the problem and determine that the combined gas law  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  is the necessary equation to use to solve the problem. Then solve for  $P_2$ :

$$\frac{0.981 \text{ atm} \times 100.21 \text{ L}}{294 \text{ K}} = \frac{P_2 \times 144.53 \text{ L}}{278.24 \text{ atm}}$$

$$P_2 = 0.644 \text{ atm}$$

30. The pressure decreases by a factor of 3.

## Glossary

**absolute zero:** temperature at which the volume of a gas would be zero according to Charles's law.

**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

**Avogadro's law:** volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

**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

**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

**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  $R = 0.08226 \text{ L atm mol}^{-1} \text{ K}^{-1}$  or  $8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$

**ideal gas law:** relation between the pressure, volume, amount, and

temperature of a gas under conditions derived by combination of the simple gas laws

**standard conditions of temperature and pressure (STP):** 273.15 K (0 °C) and 1 atm (101.325 kPa)

**standard molar volume:** volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

# 4I. 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 behavior 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 behavior 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's, 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 Behavior 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 behavior of a gas as follows:

- *Amontons'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 1).

- *Charles's 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 outweigh those of increased collision forces due to the greater kinetic energy at the higher temperature. The net result is a decrease in gas pressure.
- *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 1).
- *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 1).
- *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.



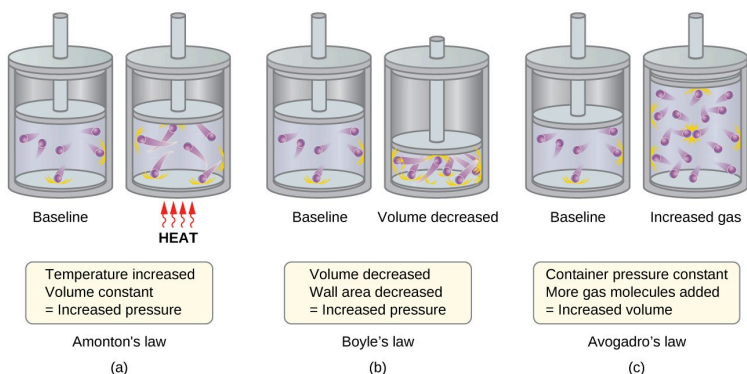


Figure 1. (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

## Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors 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 2).

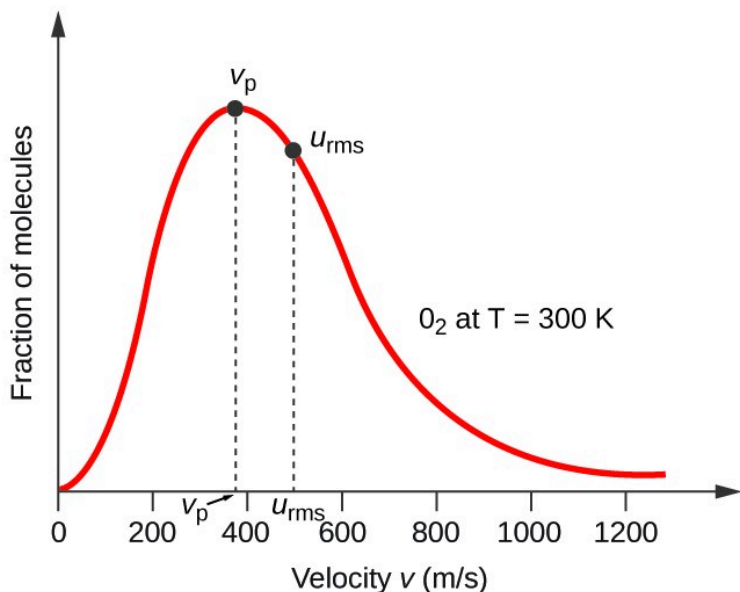


Figure 2. The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the 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.

The kinetic energy (KE) of a particle of mass ( $m$ ) and speed ( $u$ ) is given by:

$$KE = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules ( $J = \text{kg m}^2 \text{s}^{-2}$ ). 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:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$$

The average kinetic energy,  $KE_{avg}$ , is then equal to:

$$KE_{avg} = \frac{1}{2}mu_{rms}^2$$

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:

$$KE_{avg} = \frac{3}{2}RT$$

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  $8.314 \text{ J/K}$  ( $8.314 \text{ kg m}^2\text{s}^{-2}\text{K}^{-1}$ ). These two separate equations for  $KE_{avg}$  may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2}mu_{rms}^2 = \frac{3}{2}RT \quad u_{rms} = \sqrt{\frac{3RT}{m}}$$

### *Example 1: Calculation of $u_{rms}$*

Calculate the root-mean-square velocity for a nitrogen molecule at  $30^\circ\text{C}$ .

Show Answer

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  $\text{kg m}^2\text{s}^{-2}$ :

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$
$$u_{\text{rms}} = \sqrt{\frac{3(8.314\text{J/mol K})(303\text{ K})}{(0.028\text{kg/mol})}} = \sqrt{2.70 \times 10^5\text{m}^2\text{s}^{-2}} = 519\text{m/s}$$

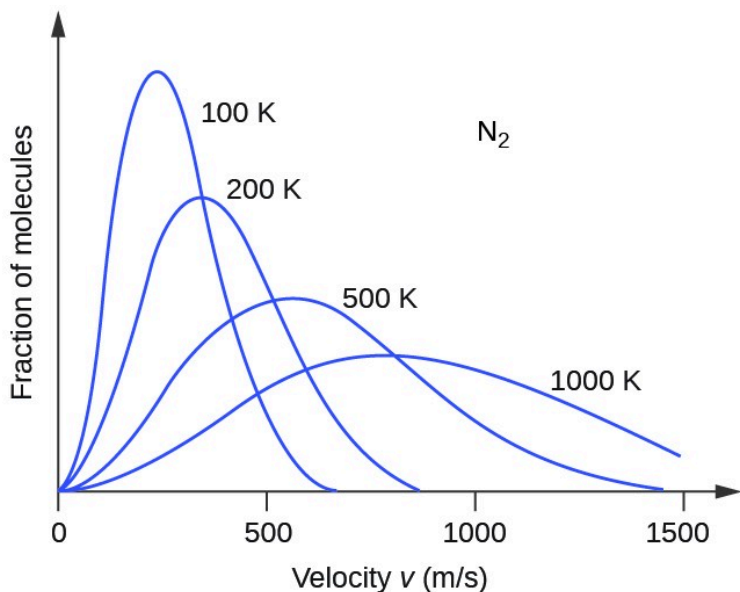
### *Check Your Learning*

Calculate the root-mean-square velocity for an oxygen molecule at  $-23^\circ\text{C}$ .

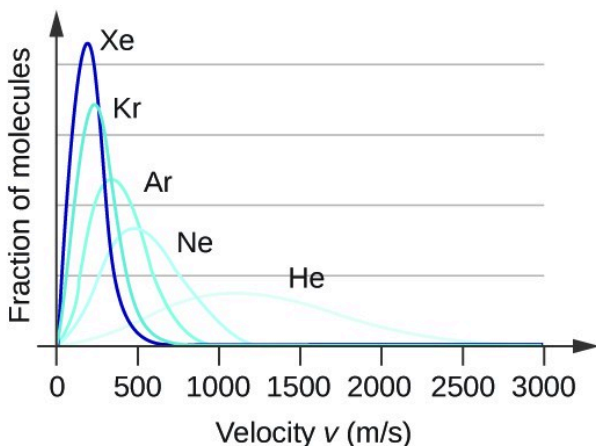
Show Answer

441 m/s

If the temperature of a gas increases, its  $\text{KE}_{\text{avg}}$  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,  $\text{KE}_{\text{avg}}$  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 behavior is illustrated for nitrogen gas in Figure 3.



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 4.



The [PhET gas simulator](#) 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.

## The Kinetic-Molecular Theory Explains the Behavior 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:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}} \quad m = \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\bar{u}^2}$$

$$\frac{\text{effusion rate A}}{\text{effusion rate B}} = \frac{u_{\text{rmsA}}}{u_{\text{rmsB}}} = \frac{\sqrt{\frac{3RT}{m_{\text{A}}}}}{\sqrt{\frac{3RT}{m_{\text{B}}}}} = \sqrt{\frac{m_{\text{B}}}{m_{\text{A}}}}$$

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 Concepts and Summary*

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. 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 velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

### Key Equations

- $u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$
- $\text{KE}_{\text{avg}} = \frac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$

### Exercises

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.
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 9.34. If the sample is cooled, will the distribution of velocities look more like that of  $\text{H}_2$  or of  $\text{H}_2\text{O}$ ? Explain your answer.
5. What is the ratio of the average kinetic energy of a  $\text{SO}_2$  molecule to that of an  $\text{O}_2$  molecule in a mixture of two gases? What is the ratio of the root mean square speeds,  $u_{\text{rms}}$ , of the two gases?
6. A 1-L sample of  $\text{CO}$  initially at STP is heated to  $546^\circ\text{C}$ , 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?
7. The root mean square speed of  $\text{H}_2$  molecules at  $25^\circ\text{C}$  is about  $1.6\text{ km/s}$ . What is the root mean square speed of a  $\text{N}_2$  molecule at  $25^\circ\text{C}$ ?
8. Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2,  $\frac{R_1}{R_2}$ , is the same at  $0^\circ\text{C}$  and  $100^\circ\text{C}$ .

#### Selected Answers

2. 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.

4.  $\text{H}_2\text{O}$ . Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

6. Both the temperature and the volume are doubled for this gas ( $n$  constant), so  $P$  remains constant.

- a. The number of collisions per unit area of the container wall is constant.
- b. The average kinetic energy doubles; it is proportional to temperature.
- c. The root mean square speed increases to  $\sqrt{2}$  times its initial value;  $u_{\text{rms}}$  is proportional to  $\sqrt{\text{KE}_{\text{avg}}}$ .

8. The rate at which a gas will diffuse,  $R$ , is proportional to  $u_{\text{rms}}$ , the root mean square speed of its molecules. The square of this value, in turn, is proportional to the average kinetic energy. The average kinetic energy is:

$$\overline{\text{KE}}_{\text{avg}} = kT$$

For two different gases, 1 and 2, the constant of proportionality can be represented as  $k_1$  and  $k_2$ , respectively. Thus,

$$\frac{R_1}{R_2} = \frac{k_1 \sqrt{T}}{k_2 \sqrt{T}}$$

As a result of this relationship, no matter at which temperature diffusion occurs, the temperature term will cancel out of the equation and the ratio of rates will be the same.

## Exercises

1. 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?
2. 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?
3. 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?
4. The average temperature of the gas in a hot air balloon is  $1.30 \times 10^2$  °F. Calculate its density, assuming the molar mass equals that of dry air.
5. 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)?
6. An average balloon has a diameter of 60 feet and a volume of  $1.1 \times 10^5$  ft<sup>3</sup>. 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?
7. A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO<sub>2</sub> and H<sub>2</sub>O gas is produced by the combustion of this propane?
8. 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?

Show Answer

1. equal, because the balloon is free to expand until the pressures are equalized
2. less than the density outside
3. assume three-place accuracy throughout unless greater accuracy is stated:

$$\text{molar mass} = \frac{DRT}{P} = 1.2256 \cancel{\text{g L}^{-1}} \times \frac{0.08206 \cancel{\text{L atm mol}^{-1} \text{K}^{-1}} \times 293.15 \cancel{\text{K}}}{1.00 \cancel{\text{atm}}} = 29.48 \text{ g mol}^{-1}$$

4. convert the temperature to °C; then use the ideal gas law:

$$^{\circ}\text{C} = \frac{5}{9}(\text{F} - 32) = \frac{5}{9}(130 - 32) = 54.44^{\circ}\text{C} = 327.6\text{K}$$

$$D = \frac{MP}{RT} = 29.48 \cancel{\text{g mol}^{-1}} \times \frac{1.00 \cancel{\text{atm}}}{0.08206 \cancel{\text{L atm mol}^{-1} \text{K}^{-1}} \times 327.6 \cancel{\text{K}}} = 1.0966 \text{ g L}^{-1}$$

5.  $1.2256 \text{ g/L} - 1.09966 \text{ g/L} = 0.129 \text{ g/L};$
6. calculate the volume in liters, multiply the volume by the density difference to find the lifting capacity of the balloon, subtract the weight of the balloon after converting to pounds:

$$1.1 \times 10^5 \text{ft}^3 \times \left(\frac{12 \text{ in}}{91 \text{ ft}}\right)^3 \times \left(\frac{2.54 \text{ cm}}{\text{in}}\right)^3 \times \frac{1 \text{ L}}{1000 \text{cm}^3} = 3.11 \times 10^6 \text{L}$$

$$3.11 \times 10^6 \text{ L} \times 0.129 \text{ g/L} = 4.01 \times 10^5 \text{ g}$$

$$\frac{4.01 \times 10^5 \text{ g}}{453.59 \text{ g lb}^{-1}} = 884 \text{ lb}; 884 \text{ lb} - 500 \text{ lb} = 384 \text{ lb}$$

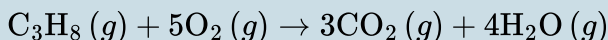
net lifting capacity = 384 lb

7. First, find the mass of propane contained in 40.0 gal. Then calculate the moles of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  produced from the balanced equation.

$$40.0 \cancel{\text{gal}} \times \frac{4(0.9463 \text{L})}{1 \cancel{\text{gal}}} = 151.4 \text{L}$$

$$\begin{aligned}
 &151.4 \cancel{\text{L}} \times 0.5005 \text{g} \cancel{\text{L}}^{-1} = 75.8 \text{g}^{\text{Molar}} \\
 &\text{mass of propane} = 3(12.011) + 8(1.00794) = 36.033 + \\
 &8.064 = 44.097 \text{ g mol}^{-1} \\
 &\frac{75.8 \cancel{\text{g}}}{44.097 \cancel{\text{g}} \text{mol}^{-1}} = 1.72 \text{mol}
 \end{aligned}$$

The reaction is



For each 1.72 mol propane, there are  $3 \times 1.72 \text{ mol} = 5.15$  mol of  $\text{CO}_2$  and  $4 \times 1.72 \text{ mol} = 6.88 \text{ mol}$   $\text{H}_2\text{O}$ . The total volume at STP =  $22.4 \text{ L} \times 12.04 = 270 \text{ L}$

8. The total heat released is determined from the heat of combustion of the propane. Using the equation in question 7,

$$\begin{aligned}
 \Delta H_{\text{combustion}}^{\circ} &= 3\Delta H_{\text{CO}_2(g)}^{\circ} + 4\Delta H_{\text{H}_2\text{O}(g)}^{\circ} - \Delta H_{\text{propane}}^{\circ} \\
 &= 3(-393.51) + 4(-241.82) - (-103.85) \\
 &= -1180.52 - 967.28 + 103.85 = -2043.96 \text{ kJ mol}^{-1}
 \end{aligned}$$

Since there is 1.72 mol propane,  $1.72 \times 2043.96 \text{ kJ mol}^{-1} = 3.52 \times 10^3 \text{ kJ}$  used for heating. This heat is used over 90 minutes, so

$$\frac{3.52 \times 10^3 \text{ kJ}}{90 \text{ min}} = 39.1 \text{ kJ min}^{-1} \text{ is released.}$$

## Glossary

**kinetic molecular theory:** theory based on simple principles and assumptions that effectively explains ideal gas behavior

**root mean square velocity ( $u_{\text{rms}}$ ):** measure of average velocity for a group of particles calculated as the square root of the average squared velocity

## 42. 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 meters 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 1). 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 1. 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).

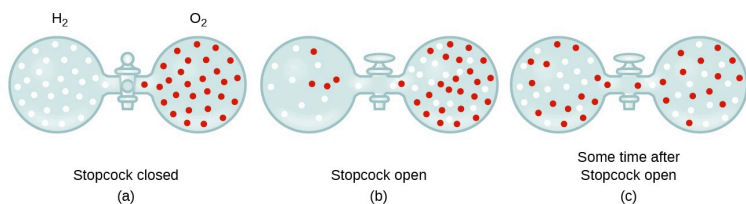


Figure 1. (a) Two gases, H<sub>2</sub> and O<sub>2</sub>, are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas, H<sub>2</sub>, passes through the opening faster than O<sub>2</sub>, so just after the stopcock is opened, more H<sub>2</sub> molecules move to the O<sub>2</sub> side than O<sub>2</sub> molecules move to the H<sub>2</sub> side. (c) After a short time, both the slower-moving O<sub>2</sub> molecules and the faster-moving H<sub>2</sub> molecules have distributed themselves evenly on both sides of the vessel.

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 2). 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.

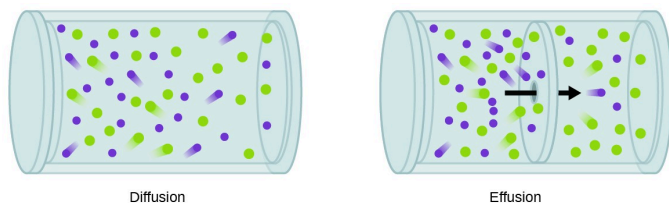


Figure 2. Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance traveled between collisions. Effectively, this means that only one particle passes through at a time.

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 3). 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:

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}}$$



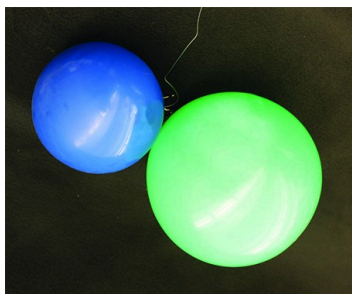


Figure 3. A balloon filled with air (the blue one) remains full overnight. A balloon filled with helium (the green one) partially deflates because the smaller, light helium atoms effuse through small holes in the rubber much more readily than the heavier molecules of nitrogen and oxygen found in air. (credit: modification of work by Mark Ott)

### Example 1: 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.

Show Answer

From Graham's law, we have:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{1.43 \text{ g L}^{-1}}}{\sqrt{0.0899 \text{ g L}^{-1}}} = \frac{1.20}{0.300} = \frac{4}{1}$$

Using molar masses:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{32 \text{ g mol}^{-1}}}{\sqrt{2 \text{ g mol}^{-1}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

### *Check Your Learning*

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?

Show Answer

52 mL/s

Here's another example, making the point about how determining times differs from determining rates.

### *Example 2: Effusion Time Calculations*

It takes 243 s for  $4.46 \times 10^{-5}$  mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take  $4.46 \times 10^{-5}$  mol Ne to effuse?

Show Answer

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.

### Check Your Learning

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 ( $\mathcal{M} = 28.2 \text{ g/mol}$ ) to deflate to  $\frac{1}{2}$  of its original volume?

Show Answer

32 h

Finally, here is one more example showing how to calculate molar mass from effusion rate data.

### *Example 3: Determining Molar Mass Using Graham's Law*

An unknown gas effuses 1.66 times more rapidly than  $\text{CO}_2$ . What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

Show Answer

From Graham's law, we have:

$$\frac{\text{rate of effusion of Unknown}}{\text{rate of effusion of CO}_2} = \frac{\sqrt{\mathcal{M}_{\text{CO}_2}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0 \text{ g/mol}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Solve:

$$\mathcal{M}_{Unknown} = \frac{44.0\text{g/mol}}{(1.66)^2} = 16.0\text{g/mol}$$

The gas could well be CH<sub>4</sub>, the only gas with this molar mass.

### *Check Your Learning*

Hydrogen gas effuses through a porous container 8.97-times faster than an unknown gas. Estimate the molar mass of the unknown gas.

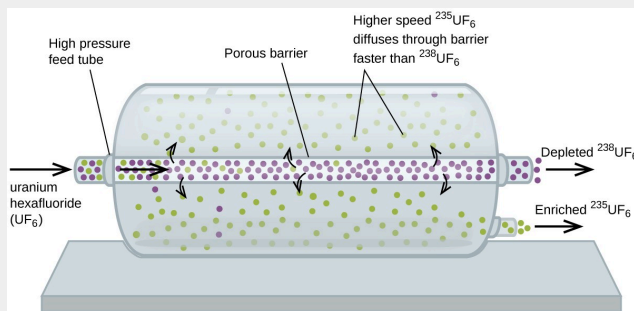
Show Answer

163 g/mol

## 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 <sup>235</sup>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% <sup>235</sup>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 ( $\text{UF}_6$ , 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  $^{235}\text{UF}_6$  molecules have a higher average speed and diffuse through the barrier a little faster than the heavier  $^{238}\text{UF}_6$  molecules. The gas that has passed through the barrier is slightly enriched in  $^{235}\text{UF}_6$  and the residual gas is slightly depleted. The small difference in molecular weights between  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  only about 0.4% enrichment, is achieved in one diffuser (Figure 4). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.



The large scale separation of gaseous  $^{235}\text{UF}_6$  from  $^{238}\text{UF}_6$  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  $\text{UF}_6$ .

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 Concepts and Summary*

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).

### *Key Equations*

- rate of diffusion =  $\frac{\text{amount of gas passing through an area}}{\text{unit of time}}$
- $$\frac{\text{rate of effusion of gas A}}{\text{rate of effusion of gas B}} = \frac{\sqrt{m_B}}{\sqrt{m_A}} = \frac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}}$$

### *Exercises*

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%?
2. Explain why the numbers of molecules are not identical in the left- and right-hand bulbs shown in the center illustration of Figure 1.
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.

4. Heavy water,  $\text{D}_2\text{O}$  (molar mass =  $20.03 \text{ g mol}^{-1}$ ), can be separated from ordinary water,  $\text{H}_2\text{O}$  (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  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ .
5. Which of the following gases diffuse more slowly than oxygen?  $\text{F}_2$ ,  $\text{Ne}$ ,  $\text{N}_2\text{O}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{NO}$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{S}$
6. During the discussion of gaseous diffusion for enriching uranium, it was claimed that  $^{235}\text{UF}_6$  diffuses  $0.4\%$  faster than  $^{238}\text{UF}_6$ . Show the calculation that supports this value. The molar mass of  $^{235}\text{UF}_6$ . =  $235.043930 + 6 \times 18.998403 = 349.034348 \text{ g/mol}$ , and the molar mass of  $^{238}\text{UF}_6$ . =  $238.050788 + 6 \times 18.998403 = 352.041206 \text{ g/mol}$ .
7. Calculate the relative rate of diffusion of  $^1\text{H}_2$  (molar mass  $2.0 \text{ g/mol}$ ) compared to that of  $^2\text{H}_2$  (molar mass  $4.0 \text{ g/mol}$ ) and the relative rate of diffusion of  $\text{O}_2$  (molar mass  $32 \text{ g/mol}$ ) compared to that of  $\text{O}_3$  (molar mass  $48 \text{ g/mol}$ ).
8. A gas of unknown identity diffuses at a rate of  $83.3 \text{ mL/s}$  in a diffusion apparatus in which carbon dioxide diffuses at the rate of  $102 \text{ mL/s}$ . 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  $87.0 \text{ cm}$  long, a white ring of  $\text{NH}_4\text{Cl}$  forms where gaseous  $\text{NH}_3$  and gaseous  $\text{HCl}$  first come into contact. (Hint: Calculate the rates of diffusion for

both  $\text{NH}_3$  and  $\text{HCl}$ , and find out how much faster  $\text{NH}_3$  diffuses than  $\text{HCl}$ .)

$\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$  At approximately what distance from the ammonia moistened plug does this occur?

#### Selected Answers

1. Use the rate of effusion equation:

$$\frac{6 \text{ hours}}{t} = \sqrt{\frac{4}{2}}t = \frac{6 \text{ hours}}{1.4} = 4.2 \text{ hours}$$

3. 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:

$$\left( \frac{\text{rate A}}{\text{rate B}} \right) = \left( \frac{\text{molar mass of B}}{\text{molar mass of A}} \right)^{1/2} \text{. Both A}$$

and B are in the same container at the same temperature, and therefore will have the same kinetic energy:

$$\begin{aligned} \text{KE}_A &= \text{KE}_B \quad \text{KE} = \frac{1}{2}mv^2 \text{ Therefore,} \\ \frac{1}{2}m_A v_A^2 &= \frac{1}{2}m_B v_B^2 \quad \frac{v_A^2}{v_B^2} = \frac{m_B}{m_A} \\ \left( \frac{v_A^2}{v_B^2} \right)^{1/2} &= \left( \frac{m_B}{m_A} \right)^{1/2} \quad \frac{v_A}{v_B} = \left( \frac{m_B}{m_A} \right)^{1/2} \end{aligned}$$

5. Gases with molecular masses greater than that of oxygen (31.9988 g/mol) will diffuse more slowly than  $\text{O}_2$ . These gases are  $\text{F}_2$  (37.9968 g/mol),  $\text{N}_2\text{O}$  (44.0128 g/mol),  $\text{Cl}_2$  (70.906 g/mol), and  $\text{H}_2\text{S}$  (34.082 g/mol).

$$\frac{R_{H_2}}{R_{D_2}} = \frac{\sqrt{\mathcal{M}_{D_2}}}{\sqrt{\mathcal{M}_{H_2}}} = \frac{\sqrt{4.0}}{\sqrt{2.0}} = \frac{2.000}{1.414} = 1.4$$

7.

$$\frac{R_{O_2}}{R_{O_3}} = \frac{\sqrt{\mathcal{M}_{O_3}}}{\sqrt{\mathcal{M}_{O_2}}} = \frac{\sqrt{48}}{\sqrt{32}} = 1.2$$

9. Rate of diffusion for  $NH_3$  is proportional to

$$\frac{1}{17.04^{1/2}} = 0.242250792 \text{ Rate of diffusion for HCl}$$

is proportional to  $\frac{1}{36.46^{1/2}} = 0.165611949$ ,

$$\left( \frac{0.242250792}{0.165611949} \right) = 1.4627.$$

## Glossary

**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)

**effusion:** transfer of gaseous atoms or molecules from a container to a vacuum through very small openings

**Graham's law of effusion:** rates of diffusion and effusion of gases are inversely proportional to the square roots of their molecular masses

**mean free path:** average distance a molecule travels between collisions

**rate of diffusion:** amount of gas diffusing through a given area over a given time

## 43. Stoichiometry of Gases

### *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 behavior 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.”

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 1: 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.

Show Answer

- $PV = nRT$

- Rearrange to get (mol/L):  $\frac{n}{v} = \frac{P}{RT}$
- 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:

$$(\mathcal{M}) \left( \frac{n}{V} \right) = \left( \frac{P}{RT} \right) (\mathcal{M})$$

- $g/L = \rho = \frac{P\mathcal{M}}{RT}$

### Check Your Learning

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?

Show Answer

$$\rho = \frac{P\mathcal{M}}{RT}$$

$$0.0847 \text{ g/L} = 760 \cancel{\text{ torr}} \times \frac{1 \cancel{\text{ atm}}}{760 \cancel{\text{ torr}}} \times \frac{\mathcal{M}}{0.0821 \text{ L} \cancel{\text{ atm}} / \text{mol K}} \times 290 \text{ K}$$

$\mathcal{M} = 2.02 \text{ g/mol}$ ; therefore, the gas must be hydrogen ( $\text{H}_2$ ,  
2.02 g/mol)

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 liter changes with temperature or pressure. Gas densities are often reported at STP.

### *Example 2: 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?

Show Answer

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:

$$85.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.136 \text{ mol C} \frac{7.136}{7.136} = 1.00 \text{ mol C}$$

$$14.3 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 14.158 \text{ mol H} \frac{14.158}{7.136} = 1.98 \text{ mol H}$$

Empirical formula is CH<sub>2</sub> [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:

$$d = \frac{PM}{RT} \frac{1.56 \text{ g}}{1.00 \text{ L}} = 0.984 \text{ atm} \times \frac{\mathcal{M}}{0.0821 \text{ L atm/mol K}} \times 323 \text{ K}$$

$$\mathcal{M} = 42.0 \text{ g/mol}, \frac{\mathcal{M}}{\text{EM}} = \frac{42.0}{14.03} = 2.99, \text{ so}$$

$(3)(\text{CH}_2) = \text{C}_3\text{H}_6$  (molecular formula).

### Check Your Learning

Acetylene, a fuel used welding torches, is comprised of 92.3% C and 7.7% H by mass. Find the empirical formula. If g of acetylene occupies a volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Show Answer

Empirical formula, CH; Molecular formula, C<sub>2</sub>H<sub>2</sub>

## 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:

$$\mathcal{M} = \frac{mRT}{PV}$$

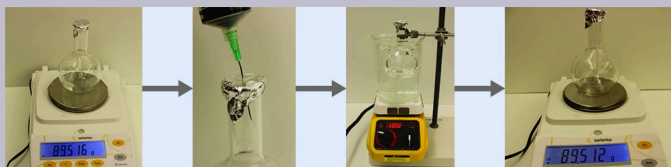
This equation can be used to derive the molar mass of a gas from measurements of its pressure, volume, temperature, and mass.



### Example 3: 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 1)



Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm<sup>3</sup> at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Show Answer

Since  $\mathcal{M} = \frac{m}{n}$  and  $n = \frac{PV}{RT}$ , substituting and rearranging gives  $\mathcal{M} = \frac{mRT}{PV}$ , then

$$M = \frac{mRT}{PV} = \frac{(0.494 \text{ g})(0.08206 \text{ L} \cdot \text{atm/mol K})(372.8 \text{ K})}{(0.976 \text{ atm})(0.129 \text{ L})} = 120 \text{ g/mol}$$

### Check Your Learning

A sample of phosphorus that weighs  $3.243 \times 10^{-2}$  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 vapor?

Show Answer

124 g/mol  $\text{P}_4$

## 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 present alone in the container (Figure 2). 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:*

$$P_{\text{Total}} = P_A + P_B + P_C + \dots = \sum_i P_i$$

In the equation  $P_{\text{Total}}$  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.

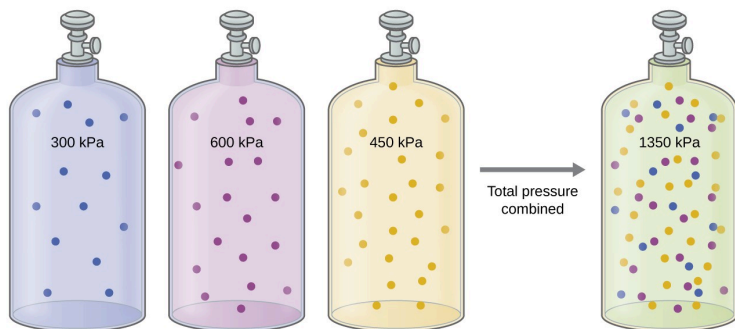


Figure 2. If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction**, 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):

$$P_A = X_A \times P_{Total} \text{ where } X_A = \frac{n_A}{n_{Total}}$$

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 4: The Pressure of a Mixture of Gases

A 10.0-L vessel contains  $2.50 \times 10^{-3}$  mol of  $H_2$ ,  $1.00 \times 10^{-3}$  mol of He, and  $3.00 \times 10^{-4}$  mol of Ne at 35 °C.

1. What are the partial pressures of each of the gases?
2. What is the total pressure in atmospheres?

Show Answer

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation,

using  $P = \frac{nRT}{V}$  :

$$P_{\text{H}_2} = \frac{(2.50 \times 10^{-3} \cancel{\text{mol}}) (0.08206 \cancel{\text{L atm mol}^{-1} \text{K}^{-1}}) (308 \text{ K})}{10.0 \cancel{\text{L}}} = 6.32 \times 10^{-3} \text{ atm}$$

$$P_{\text{He}} = \frac{(1.00 \times 10^{-3} \cancel{\text{mol}}) (0.08206 \text{ L atm } \cancel{\text{mol}^{-1} \text{K}^{-1}}) (308 \text{ K})}{10.0 \cancel{\text{L}}} = 2.53 \times 10^{-3} \text{ atm}$$

$$P_{\text{Ne}} = \frac{(3.00 \times 10^{-4} \cancel{\text{mol}}) (0.08206 \cancel{\text{L atm mol}^{-1} \text{K}^{-1}}) (308 \text{ K})}{10.0 \cancel{\text{L}}} = 7.58 \times 10^{-4} \text{ atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_{\text{T}} = P_{\text{H}_2} + P_{\text{He}} + P_{\text{Ne}} = (0.00632 + 0.00253 + 0.00076) \text{ atm} = 9.61 \times 10^{-3} \text{ atm}$$

### Check Your Learning

A 5.73-L flask at 25 °C contains 0.0388 mol of N<sub>2</sub>, 0.147 mol of CO, and 0.0803 mol of H<sub>2</sub>. What is the total pressure in the flask in atmospheres?

Show Answer

1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

### Example 5: 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.

1. What are the mole fractions of  $O_2$  and  $N_2O$ ?
2. What are the partial pressures of  $O_2$  and  $N_2O$ ?

Show Answer

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  $N_2O$ ,

$$X_{O_2} = \frac{n_{O_2}}{n_{Total}} = \frac{2.83 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.252$$

and

$$P_{O_2} = X_{O_2} \times P_{Total} = (0.252) \times 192 \text{ kPa}$$

$$P_{O_2} = X_{O_2} \times P_{Total} = 0.252 \times 192 \text{ kPa} = 48.4 \text{ kPa}$$

## Check Your Learning

What is the pressure of a mixture of 0.200 g of  $\text{H}_2$ , 1.00 g of  $\text{N}_2$ , and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Show Answer

1.87 atm

## 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 3), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

However, there is another factor we must consider when

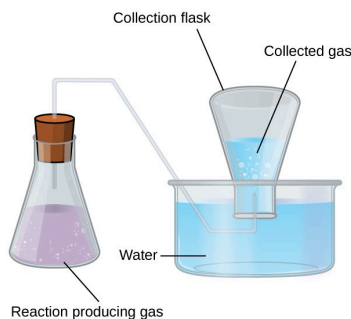


Figure 3. When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapor. The **vapor pressure of water**, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure 4); more detailed information on the temperature dependence of water vapor can be found in Table 1, and vapor pressure will be discussed in more detail in the next chapter on liquids.

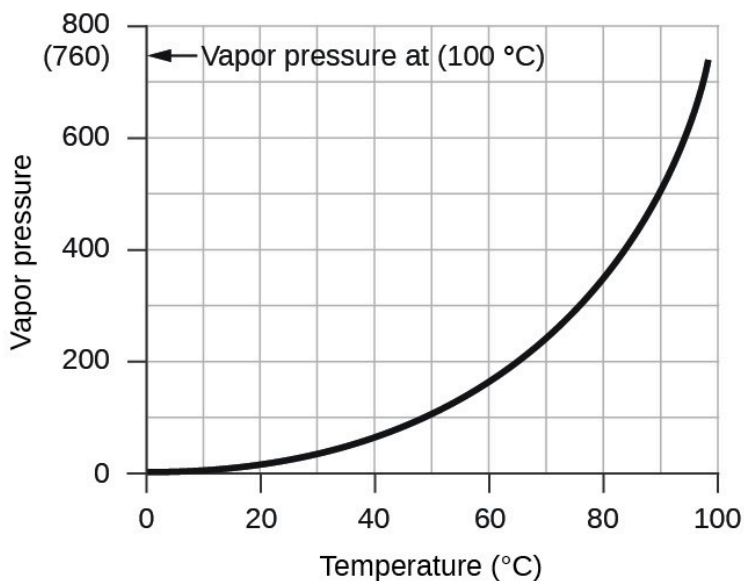


Figure 4. This graph shows the vapor pressure of water at sea level as a function of temperature.

**Table 1. Vapor Pressure of Ice and Water in Various Temperatures at Sea Level**

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (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 6: 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?

Show Answer

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:

$$P_T = P_{\text{Ar}} + P_{\text{H}_2\text{O}}$$



Rearranging this equation to solve for the pressure of argon gives:

$$P_{\text{Ar}} = P_{\text{T}} - P_{\text{H}_2\text{O}}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr ([Water Properties](#)), so:

$$P_{\text{Ar}} = 750 \text{ torr} - 25.2 \text{ torr} = 725 \text{ torr}$$

### *Check Your Learning*

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?

Show Answer

734 torr

## 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 behavior 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  $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$ , 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 5. According to Avogadro's law, equal volumes of gaseous  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ , at the same temperature and pressure, contain the same number of molecules. Because one molecule of  $\text{N}_2$  reacts with three molecules of  $\text{H}_2$  to produce two molecules of  $\text{NH}_3$ , the volume of  $\text{H}_2$  required is three times the volume of  $\text{N}_2$ , and the volume of  $\text{NH}_3$  produced is two times the volume of  $\text{N}_2$ .

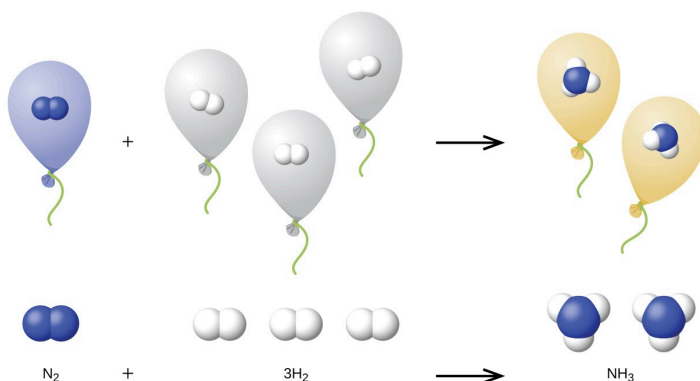


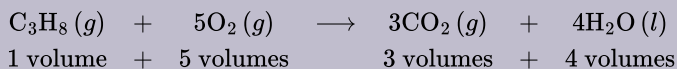
Figure 5. One volume of  $\text{N}_2$  combines with three volumes of  $\text{H}_2$  to form two volumes of  $\text{NH}_3$ .

### Example 7: Reaction of Gases

Propane,  $\text{C}_3\text{H}_8(g)$ , is used in gas grills to provide the heat for cooking. What volume of  $\text{O}_2(g)$  measured at  $25^\circ\text{C}$  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.

Show Answer

The ratio of the volumes of  $\text{C}_3\text{H}_8$  and  $\text{O}_2$  will be equal to the ratio of their coefficients in the balanced equation for the reaction:



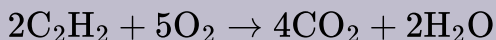
From the equation, we see that one volume of  $\text{C}_3\text{H}_8$  will react with five volumes of  $\text{O}_2$ :

$$2.7 \cancel{\text{L C}_3\text{H}_8} \times \frac{5 \text{ L O}_2}{1 \cancel{\text{L C}_3\text{H}_8}} = 13.5 \text{ L O}_2$$

A volume of 13.5 L of O<sub>2</sub> will be required to react with 2.7 L of C<sub>3</sub>H<sub>8</sub>.

### Check Your Learning

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C<sub>2</sub>H<sub>2</sub>, at 0°C and 1 atm. How many tanks of oxygen, each providing  $7.00 \times 10^3$  L of O<sub>2</sub> at 0 °C and 1 atm, will be required to burn the acetylene?

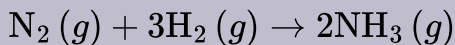


Show Answer

3.34 tanks ( $2.34 \times 10^4$  L)

### Example 8: 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<sub>2</sub>(g), measured under the same conditions, was required to prepare this amount of ammonia by reaction with N<sub>2</sub>?



Show Answer

Because equal volumes of  $\text{H}_2$  and  $\text{NH}_3$  contain equal numbers of molecules and each three molecules of  $\text{H}_2$  that react produce two molecules of  $\text{NH}_3$ , the ratio of the volumes of  $\text{H}_2$  and  $\text{NH}_3$  will be equal to 3:2. Two volumes of  $\text{NH}_3$ , in this case in units of billion  $\text{ft}^3$ , will be formed from three volumes of  $\text{H}_2$ :

$$683 \text{ billion ft}^3 \text{NH}_3 \times \frac{3 \text{ billion ft}^3 \text{H}_2}{2 \text{ billion ft}^3 \text{NH}_3} = 1.02 \times 10^3 \text{ billion ft}^3 \text{H}_2$$

The manufacture of 683 billion  $\text{ft}^3$  of  $\text{NH}_3$  required 1020 billion  $\text{ft}^3$  of  $\text{H}_2$ . (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

### *Check Your Learning*

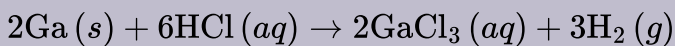
What volume of  $\text{O}_2(g)$  measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene,  $\text{C}_2\text{H}_4(g)$ , measured under the same conditions of temperature and pressure? The products are  $\text{CO}_2$  and water vapor.

Show Answer

51.0 L

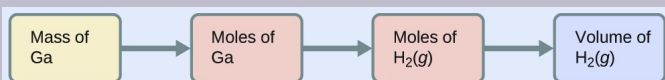
### *Example 9: Volume of Gaseous Product*

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?



Show Answer

To convert from the mass of gallium to the volume of  $\text{H}_2(g)$ , we need to do something like this:



The first two conversions are:

$$8.88 \text{ g Ga} \times \frac{1 \text{ mol Ga}}{69.723 \text{ g Ga}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Ga}} = 0.191 \text{ mol H}_2$$

Finally, we can use the ideal gas law:

$$V_{\text{H}_2} = \left( \frac{nRT}{P} \right)_{\text{H}_2} = \frac{0.191 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.951 \text{ atm}} = 4.94 \text{ L}$$

### Check Your Learning

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of  $\text{SO}_2$  at  $343^\circ\text{C}$  and  $1.21 \text{ atm}$  is produced by burning  $1.00 \text{ kg}$  of sulfur in oxygen?

Show Answer

$$1.30 \times 10^3 \text{ L}$$

## 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 favorable 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 6).

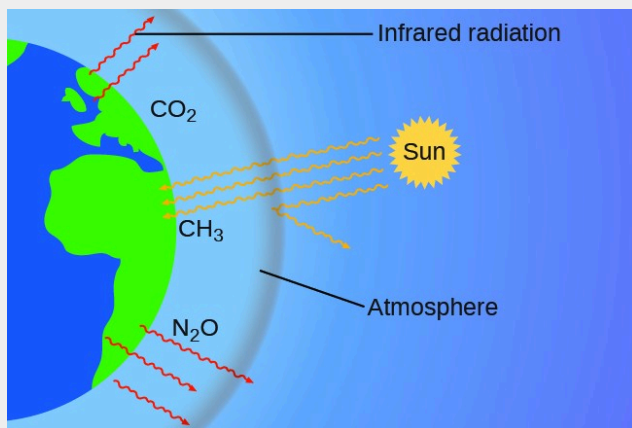
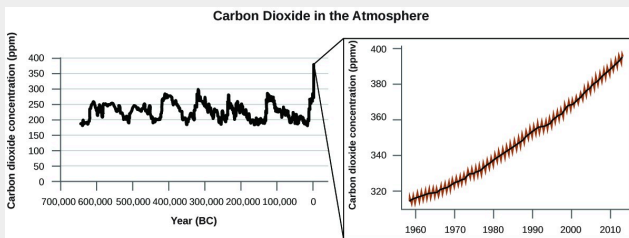


Figure 6. Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of  $\text{CO}_2$  are caused by human activity, with fossil fuel burning accounting for about  $\frac{3}{4}$  of the recent increase in  $\text{CO}_2$ . Reliable data from ice cores reveals that  $\text{CO}_2$  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  $\text{CO}_2$  concentration has increased from historical levels of below 300 ppm to almost 400 ppm today (Figure 7).





[Click here to see a 2-minute video from the Environmental Protection Agency](#) explaining greenhouse gases and global warming.

## Portrait of a Chemist: Susan Solomon

Atmospheric and climate scientist Susan Solomon (Figure 8) 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 honors 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.



Figure 8. Susan Solomon's research focuses on climate change and has been instrumental in determining the cause of the ozone hole over Antarctica. (credit: National Oceanic and Atmospheric Administration)

## *Key Concepts and Summary*

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.

### *Key Equations*

- $P_{\text{Total}} = P_A + P_B + P_C + \dots = \sum_i P_i$
- $P_A = X_A P_{\text{Total}}$
- $X_A = \frac{n_A}{n_{\text{Total}}}$

## *Exercises*

1. What is the density of laughing gas, dinitrogen monoxide,  $\text{N}_2\text{O}$ , at a temperature of 325 K and a pressure of 113.0 kPa?

2. Calculate the density of Freon 12,  $\text{CF}_2\text{Cl}_2$ , at  $30.0^\circ\text{C}$  and  $0.954\text{ atm}$ .
3. Which is denser at the same temperature and pressure, dry air or air saturated with water vapor? Explain.
4. A cylinder of  $\text{O}_2(g)$  used in breathing by emphysema patients has a volume of  $3.00\text{ L}$  at a pressure of  $10.0\text{ atm}$ . If the temperature of the cylinder is  $28.0^\circ\text{C}$ , what mass of oxygen is in the cylinder?
5. What is the molar mass of a gas if  $0.0494\text{ g}$  of the gas occupies a volume of  $0.100\text{ L}$  at a temperature  $26^\circ\text{C}$  and a pressure of  $307\text{ torr}$ ?
6. What is the molar mass of a gas if  $0.281\text{ g}$  of the gas occupies a volume of  $125\text{ mL}$  at a temperature  $126^\circ\text{C}$  and a pressure of  $777\text{ torr}$ ?
7. How could you show experimentally that the molecular formula of propene is  $\text{C}_3\text{H}_6$ , not  $\text{CH}_2$ ?
8. The density of a certain gaseous fluoride of phosphorus is  $3.93\text{ g/L}$  at STP. Calculate the molar mass of this fluoride and determine its molecular formula.
9. Consider this question: What is the molecular formula of a compound that contains  $39\%\text{ C}$ ,  $45\%\text{ N}$ , and  $16\%\text{ H}$  if  $0.157\text{ g}$  of the compound occupies  $125\text{ mL}$  with a pressure of  $99.5\text{ kPa}$  at  $22^\circ\text{C}$ ?
  - a. Outline the steps necessary to answer the question.
  - b. Answer the question.
10. A  $36.0\text{-L}$  cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains  $350\text{ g CO}_2$ ,  $805\text{ g O}_2$ , and  $4,880\text{ g N}_2$ . What is the

pressure in the flask in atmospheres, in torr, and in kilopascals?

11. A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO<sub>2</sub>, 12.0% O<sub>2</sub>, and the remainder N<sub>2</sub> 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<sub>4</sub>, 8.9% C<sub>2</sub>H<sub>6</sub>, and 1.1% C<sub>3</sub>H<sub>8</sub> 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.)
13. A mixture of 0.200 g of H<sub>2</sub>, 1.00 g of N<sub>2</sub>, 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 behavior.
14. Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O<sub>2</sub> is not. If enough O<sub>2</sub> is added to a cylinder of H<sub>2</sub> at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive?
15. A commercial mercury vapor analyzer can detect, in air, concentrations of gaseous Hg atoms (which are poisonous) as low as  $2 \times 10^{-6}$  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

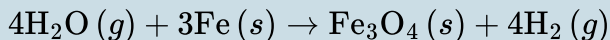
temperature of 18 °C. What is the pressure of the carbon monoxide? (See Table 9.2 for the vapor pressure of water.)

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:

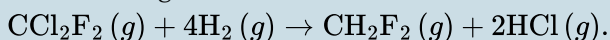


- a. Outline the steps necessary to answer the following question: What volume of O<sub>2</sub> at 23° C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?
- b. Answer the question.
19. Cavendish prepared hydrogen in 1766 by the novel method of passing steam through a red-hot gun barrel:



- a. Outline the steps necessary to answer the following question: What volume of H<sub>2</sub> at a pressure of 745 torr and a temperature of 20 °C can be prepared from the reaction of 15.0 g of H<sub>2</sub>O?
- b. Answer the question.
20. The chlorofluorocarbon CCl<sub>2</sub>F<sub>2</sub> can be recycled into a different compound by reaction with hydrogen to produce CH<sub>2</sub>F<sub>2</sub>(g), a compound useful in chemical

manufacturing:



- 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 ( $1.000 \times 10^3$  kg) of  $\text{CCl}_2\text{F}_2$ ?
  - b. Answer the question.
21. Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide ( $\text{NaN}_3$ ). 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,  $\text{CaO}$ , is produced by heating calcium carbonate,  $\text{CaCO}_3$ ; 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 ( $1.000 \times 10^3$  kg) of calcium carbonate?
  - b. Answer the question.
23. Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas,  $\text{C}_2\text{H}_2$ , and solid calcium hydroxide were formed by the reaction of calcium carbide,  $\text{CaC}_2$ , 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.

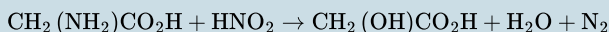
- a. Outline the steps necessary to answer the following question: What volume of  $\text{C}_2\text{H}_2$  at 1.005 atm and  $12.2^\circ\text{C}$  is formed by the reaction of 15.48 g of  $\text{CaC}_2$  with water?
  - b. Answer the question.
24. Calculate the volume of oxygen required to burn 12.00 L of ethane gas,  $\text{C}_2\text{H}_6$ , to produce carbon dioxide and water, if the volumes of  $\text{C}_2\text{H}_6$  and  $\text{O}_2$  are measured under the same conditions of temperature and pressure.
25. What volume of  $\text{O}_2$  at STP is required to oxidize 8.0 L of  $\text{NO}$  at STP to  $\text{NO}_2$ ? What volume of  $\text{NO}_2$  is produced at STP?
26. Consider the following questions:
- a. What is the total volume of the  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$  at  $600^\circ\text{C}$  and 0.888 atm produced by the combustion of 1.00 L of  $\text{C}_2\text{H}_6(g)$  measured at STP?
  - b. What is the partial pressure of  $\text{H}_2\text{O}$  in the product gases?
27. Methanol,  $\text{CH}_3\text{OH}$ , is produced industrially by the following reaction:
- $$\text{CO}(g) + 2\text{H}_2(g) \xrightarrow{\text{copper catalyst } 300^\circ\text{C}, 300\text{ atm}} \text{CH}_3\text{OH}(g)$$
- 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<sub>2</sub> to BaO and O<sub>2</sub>?

29. A 2.50-L sample of a colorless gas at STP decomposed to give 2.50 L of N<sub>2</sub> and 1.25 L of O<sub>2</sub> at STP. What is the colorless gas?
30. Ethanol, C<sub>2</sub>H<sub>5</sub>OH, is produced industrially from ethylene, C<sub>2</sub>H<sub>4</sub>, by the following sequence of reactions:
- $$3\text{C}_2\text{H}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{C}_2\text{H}_5\text{HSO}_4 + (\text{C}_2\text{H}_5)_2\text{SO}_4$$
- $$\text{C}_2\text{H}_5\text{HSO}_4 + (\text{C}_2\text{H}_5)_2\text{SO}_4 + 3\text{H}_2\text{O} \rightarrow 3\text{C}_2\text{H}_5\text{OH} + 2\text{H}_2\text{SO}_4$$
- 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%?
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.)
33. One method of analyzing amino acids is the van Slyke method. The characteristic amino groups (-NH<sub>2</sub>) in protein material are allowed to react with nitrous acid, HNO<sub>2</sub>, to form N<sub>2</sub> 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,  $\text{CH}_2(\text{NH}_2)\text{COOH}$ , was analyzed by the van Slyke method and yielded 3.70 mL of  $\text{N}_2$  collected over water at a pressure of 735 torr and 29 °C. What was the percentage of glycine in the sample?



#### Selected Answers

2.

$$\rho = \frac{PM}{RT} = \frac{0.954 \cancel{\text{atm}} [12.011 + 2(18.9954) + 2(35.453)] \text{g} \cancel{\text{mol}^{-1}}}{0.08206 \text{ L} \cancel{\text{atm}} \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}} \times 303.15 \text{ K}} = 4.64 \text{ gL}^{-1}$$

4.

$$\text{mass O}_2 = \frac{(31.9988 \text{ g} \cancel{\text{mol}^{-1}}) (10.0 \cancel{\text{atm}}) (3.00 \cancel{\text{L}})}{(0.08206 \cancel{\text{L}} \cancel{\text{atm}} \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}}) (301.15 \cancel{\text{K}})} = 38.8 \text{ g}$$

6. From the ideal gas law,  $PV = nRT$ , set

$$n = \frac{\text{mass}}{\text{molar mass}} \text{ and solve the molar mass.}$$

$$\text{molar mass} = \frac{(0.281 \text{ g}) (0.08206 \cancel{\text{L}} \cancel{\text{atm}} \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}}) (399.15 \cancel{\text{K}})}{\left( \frac{777 \cancel{\text{torr}}}{760 \cancel{\text{torr}} \cancel{\text{atm}^{-1}}} \right) (0.125 \cancel{\text{L}})} = 72.0 \text{ gmol}^{-1}$$

$$8. \mathcal{M} = \frac{mRT}{PV} D = \frac{m}{V} \mathcal{M} = \frac{DRT}{P}$$

$$\mathcal{M} = \frac{3.93 \text{ gL}^{-1} (0.08206 \cancel{\text{L}} \cancel{\text{atm}} \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}}) (273.15 \cancel{\text{K}})}{1.00 \cancel{\text{atm}}} = 88.1 \text{ gmol}^{-1}$$

$$\mathcal{M}_{\text{phosphorous}} = 30.97376 \text{ g/mol}$$

$$\mathcal{M}_{\text{fluorine}} = 18.998403 \text{ g/mol}$$

molecular formula:	phosphorous:	30.97376
	fluorine:	<u>3 (18.998403)</u>
		87.968969

The molecular formula is  $\text{PF}_3$ .

To find this answer you can either use trial and error, or you can realize that since phosphorus is in group 5, it can fill its valence shell by forming three bonds. Fluorine, being in group 7, needs to form only one bond to fill its shell. Thus it makes sense to start with  $\text{PF}_3$  as a probable formula.

10. Calculate the moles of each gas present and from that, calculate the pressure from the ideal gas law. Assume  $25^\circ\text{C}$ . The calibration gas contains:

$$\begin{aligned}\frac{350 \cancel{\text{g}} \text{CO}_2}{44.0098 \cancel{\text{g}} \text{mol}^{-1} \text{CO}_2} &= 7.953 \text{ mol CO}_2 \\ \frac{805 \cancel{\text{g}} \text{O}_2}{31.9988 \cancel{\text{g}} \text{mol}^{-1} \text{O}_2} &= 25.157 \text{ mol O}_2 \\ \frac{4880 \cancel{\text{g}} \text{N}_2}{28.01348 \cancel{\text{g}} \text{mol}^{-1} \text{N}_2} &= 174.202 \text{ mol N}_2\end{aligned}$$

$$\text{Total moles} = 7.953 + 25.157 + 174.202 = 207.312 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{207.312 \cancel{\text{mol}} \times 0.08206 \cancel{\text{L}} \text{atm} \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}} \times 298.15 \cancel{\text{K}}}{36.0 \cancel{\text{L}}} = 141 \text{ atm}$$

12. Since these are percentages of the total pressure, the partial pressure can be calculated as follows:

- $\text{CH}_4$ : 90% of 307.2 kPa =  $0.900 \times 307.2 = 276 \text{ kPa}$
- $\text{C}^2\text{H}^6$ : 8.9% of 307.2 kPa =  $0.089 \times 307.2 = 27 \text{ kPa}$
- $\text{C}^3\text{H}^8$ : 1.1% of 307.2 kPa =  $0.011 \times 307.2 = 3.4 \text{ kPa}$

14. The oxygen increases the pressure within the tank to (34.5 atm – 33.2 atm =) 1.3 atm. The percentage  $\text{O}_2$  on a mole basis is  $\frac{1.3}{34.5} \times 100\% = 3.77\%$ . The mixture is explosive. However, the percentage is given as a weight percent. Converting to a mass basis increases the

percentage of oxygen even more, so the mixture is still explosive.

16. The vapor pressure of water at 18 °C is 15.5 torr. Subtract the vapor pressure of water from the total pressure to find the pressure of the carbon monoxide:

$$P_T = P_{\text{gas}} + P_{\text{water}}$$

Rearrangement gives:  $P_T - P_{\text{water}} = P_{\text{gas}}$

$$756 \text{ torr} - 15.5 \text{ torr} = 740 \text{ torr}$$

18. The answers are as follows:

- a. Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O<sub>2</sub> produced by decomposition of this amount of HgO; and determine the volume of O<sub>2</sub> from the moles of O<sub>2</sub>, temperature, and pressure.

$$\text{b. } 5.36 \text{ g } \cancel{\text{HgO}} \times \frac{1 \text{ mol HgO}}{(200.59 + 15.9994) \text{ g } \cancel{\text{HgO}}} = 0.0247 \text{ mol HgO}$$

$$0.0247 \text{ mol } \cancel{\text{HgO}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol } \cancel{\text{HgO}}} = 0.01235 \text{ mol O}_2$$

$$PV = nRT$$

$$P = 0.975 \text{ atm}$$

$$T = (23.0 + 273.15) \text{ K}$$

$$V = \frac{nRT}{P} = \frac{0.01235 \text{ mol} \left( 0.08206 \text{ L } \cancel{\text{atm}} \cancel{\text{mol}^{-1}} \cancel{\text{K}^{-1}} \right) (296.15 \text{ K})}{0.975 \text{ atm}} = 0.308 \text{ L}$$

20. The answers are as follows:

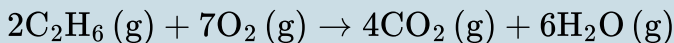
- a. Determine the molar mass of CCl<sub>2</sub>F<sub>2</sub>. From the balanced equation, calculate the moles of H<sub>2</sub> needed for the complete reaction. From the ideal gas law, convert moles of H<sub>2</sub> into volume.

$$\begin{aligned} \text{b. Molar mass of CCl}_2\text{F}_2 &= 12.011 + 2 \times 18.9984 + 2 \times 35.4527 = 120.913 \text{ g/mol} \\ \text{molH}_2 &= 1.000 \times 10^6 \text{ g} \times \frac{1 \text{ molCCl}_2\text{F}_2}{120.913 \text{ g}} \times \frac{4 \text{ molH}_2}{1 \text{ molCCl}_2\text{F}_2} = 3.308 \times 10^4 \text{ mol} \\ V &= \frac{nRT}{P} = \frac{(3.308 \times 10^4 \text{ mol}) (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (308.65 \text{ K})}{225 \text{ atm}} = 3.72 \times 10^3 \text{ L} \end{aligned}$$

22. The answers are as follows:

$$\begin{aligned} \text{a. Balance the equation. Determine the grams of CO}_2 \text{ produced and the number of moles. From the ideal gas law, determine the volume of gas.} \\ \text{b. CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \\ \text{massCO}_2 &= 1.00 \times 10^6 \text{ g} \times \frac{1 \text{ molCaCO}_3}{100.087 \text{ g}} \times \frac{44.01 \text{ gCO}_2}{1 \text{ molCO}_2} \times \frac{1 \text{ molCO}_2}{1 \text{ molCaCO}_3} = 4.397 \times 10^5 \text{ g} \\ \text{molCO}_2 &= \frac{4.397 \times 10^5 \text{ g}}{44.01 \text{ gmol}^{-1}} = 9991 \text{ mol} \\ V &= \frac{nRT}{P} = \frac{(9991 \text{ mol}) (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (875 \text{ K})}{0.966 \text{ atm}} = 7.43 \times 10^5 \text{ L} \end{aligned}$$

24.

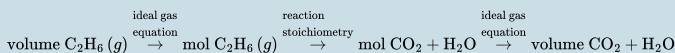


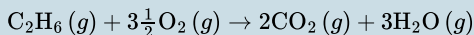
From the balanced equation, we see that 2 mol of C<sub>2</sub>H<sub>6</sub> requires 7 mol of O<sub>2</sub> to burn completely. Gay-Lussac's law states that gases react in simple proportions by volume. As the number of liters is proportional to the number of moles,

$$\begin{aligned} \frac{12.00 \text{ L}}{2 \text{ molC}_2\text{H}_6} &= \frac{V(\text{O}_2)}{7 \text{ molO}_2} \\ V(\text{O}_2) &= \frac{12.00 \text{ L} \times 7}{2} = 42.00 \text{ L} \end{aligned}$$

26. The answers are as follows:

(a) The scheme to solve this problem is:





$$1. n(\text{C}_2\text{H}_6) = \frac{PV}{RT} = \frac{1.00 \text{ atm} \times 1.00 \cancel{\text{L}}}{0.08206 \cancel{\text{L}} \text{ atm mol}^{-1} \text{ K}^{-1} (273.15 \text{ K})} = 0.0446 \text{ mol}$$

$$2. 0.0446 \cancel{\text{mol C}_2\text{H}_6} \times \frac{5 \text{ mol products}}{1 \cancel{\text{mol C}_2\text{H}_6}} = 0.223 \text{ mol products}$$

$$3. V = nRT = \frac{(0.223 \cancel{\text{mol}})(0.08206 \cancel{\text{L atm mol}^{-1} \text{ K}^{-1}})(873.15 \text{ K})}{0.888 \text{ atm}} = 18.0 \text{ L}$$

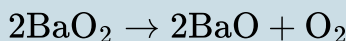
(b) First, calculate the mol H<sub>2</sub>O produced:

$$0.0446 \text{ mol C}_2\text{H}_6 \times \frac{3 \text{ mol products}}{1 \text{ mol C}_2\text{H}_6} = 0.1338 \text{ mol}$$

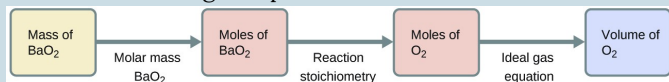
Second, calculate the pressure of H<sub>2</sub>O:

$$P = \frac{nRT}{V} = \frac{(0.1338 \cancel{\text{mol}})(0.8206 \cancel{\text{L atm mol}^{-1} \text{ K}^{-1}})(873.15 \text{ K})}{18.0 \cancel{\text{L}}} = 5.53 \text{ atm}$$

28. First, we must write a balanced equation to establish the stoichiometry of the reaction:



We are given the mass of BaO<sub>2</sub> that decomposes, so the scheme for solving this problem will be:



$$\text{Mass}(\text{BaO}_2) = 137.33 + 2(15.9994) = 169.33 \text{ g/mol}$$

$$n(\text{O}_2) = 129.7 \text{ g BaO}_2 \times \frac{1 \text{ mol BaO}_2}{169.33 \text{ g BaO}_2} \times \frac{1 \text{ mol O}_2}{2 \text{ mol BaO}_2} = 0.3830 \text{ mol O}_2$$

$$V(\text{O}_2) = \frac{nRT}{P} = \frac{0.3830 \text{ mol} (8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}) (423.0 \text{ K})}{127.4 \text{ kPa}} = 10.57 \text{ L O}_2$$

30. At 90.1% conversion, a  $1.000 \times 10^6 \text{ g}$  final yield would

$$\text{require a } \left( \frac{1.000 \times 10^6}{0.901} \right) = 1.1099 \times 10^6 \text{ g}$$

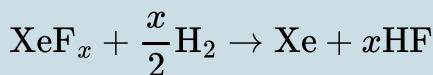
theoretical yield.

3C<sub>2</sub>H<sub>4</sub> produces 3C<sub>2</sub>H<sub>5</sub>OH, giving a 1:1 ratio:

$$\text{mol (C}_2\text{H}_4) = 1.1099 \times 10^6 \cancel{\text{gC}_2\text{H}_5\text{OH}} \times \frac{1 \cancel{\text{molC}_2\text{H}_5\text{OH}}}{46.069 \cancel{\text{gC}_2\text{H}_5\text{OH}}} \times \frac{1 \text{ molC}_2\text{H}_4}{1 \cancel{\text{molC}_2\text{H}_5\text{OH}}} = 2.409 \times 10^4 \text{mol}$$

$$V(\text{C}_2\text{H}_4) = 22.4 \text{ L/mol} \times 2.409 \times 10^4 \text{ mol} = 5.40 \times 10^5 \text{ L}$$

32. The reaction is:



The pressure of  $\text{H}_2$  that reacts is  $48 \text{ torr} - 24 \text{ torr} = 24 \text{ torr}$

The number of moles of gas is proportional to the partial pressures. The reaction used 24 torr of  $\text{XeF}_x$  and 24 torr of

$$\text{H}_2 \text{ so: } \frac{x}{2} = 1 \text{ and } x = 2$$

The formula for the xenon compound is  $\text{XeF}_2$ .

Immediately after the  $\text{H}_2$  is added (before the reaction):

$$\begin{aligned} P_{\text{Total}} &= P_{\text{XeF}_2} + P_{\text{H}_2} \\ P_{\text{H}_2} &= P_{\text{Total}} - P_{\text{XeF}_2} \\ &= 72 \text{ torr} - 24 \text{ torr} \\ &= 48 \text{ torr} \end{aligned}$$

After the reaction:

$$P_{\text{Xe}} = 24 \text{ torr} \quad (1 \text{ molXeF}_x \rightarrow 1 \text{ mol Xe})$$

And the partial pressure of unreacted  $\text{H}_2$  is:

$$\begin{aligned} P_{\text{H}_2} &= P_{\text{Total}} - P_{\text{Xe}} \\ &= 48 \text{ torr} - 24 \text{ torr} \\ &= 24 \text{ torr} \end{aligned}$$

## Glossary

**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.

**mole fraction:** concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

**partial pressure:** pressure exerted by an individual gas in a mixture

**vapor pressure of water:** pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature



PART XI

# NUCLEAR REACTIONS



# 44. Nuclear Structure and Stability

## *Learning Objectives*

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

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

**Nuclear chemistry** is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of  ${}^1_1\text{H}$ , neutrons. Recall that the number of protons in the nucleus is called the atomic number ( $Z$ ) of the element, and the sum of the number of protons and the number of neutrons is the mass number ( $A$ ). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation  ${}^A_Z\text{X}$ , where  $\text{X}$  is the symbol for the element,  $A$  is the mass number, and  $Z$  is the atomic number (for example,  ${}^{14}_{16}\text{C}$ ). Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example,  ${}^{14}_{16}\text{C}$  is called “carbon-14.”

Protons and neutrons, collectively called **nucleons**, are packed

together tightly in a nucleus. With a radius of about  $10^{-15}$  meters, a nucleus is quite small compared to the radius of the entire atom, which is about  $10^{-10}$  meters. Nuclei are extremely dense compared to bulk matter, averaging  $1.8 \times 10^{14}$  grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of  $22.6 \text{ g/cm}^3$ . If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately  $6.4 \times 10^6$  meters, 30,000 times larger). Example 1 demonstrates just how great nuclear densities can be in the natural world.

### *Example 1: Density of a Neutron Star*

Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star's outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass =  $M_{\odot}$  = mass of the sun =  $1.99 \times 10^{30} \text{ kg}$ ) and a diameter of 26 km.

1. What is the density of this neutron star?
2. How does this neutron star's density compare to the density of a uranium nucleus, which has a diameter of about 15 fm ( $1 \text{ fm} = 10^{-15} \text{ m}$ )?

Show Answer

We can treat both the neutron star and the U-235

nucleus as spheres. Then the density for both is given by:

$$d = \frac{m}{V} \text{ with } V = \frac{4}{3}\pi r^3$$

1. The radius of the neutron star is

$$\frac{1}{2} \times 26 \text{ km} = \frac{1}{2} \times 2.6 \times 10^4 \text{ m} = 1.3 \times 10^4 \text{ m}$$

, so the density of the neutron star is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{2.4 (1.99 \times 10^{30} \text{ kg})}{\frac{4}{3}\pi (1.3 \times 10^4 \text{ m})^3} = 5.2 \times 10^{17} \text{ kg/m}^3$$

2. The radius of the U-235 nucleus is

$$\frac{1}{2} \times 15 \times 10^{-15} \text{ m} = 7.5 \times 10^{-15} \text{ m, so}$$

the density of the U-235 nucleus is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{235 \text{ amu} \left( \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)}{\frac{4}{3}\pi (7.5 \times 10^{-15} \text{ m})^3} = 2.2 \times 10^{17} \text{ kg/m}^3$$

These values are fairly similar (same order of magnitude), but the nucleus is more than twice as dense as the neutron star.

### *Check Your Learning*

Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of 1.75 fm (1 fm =  $1 \times 10^{-15}$  m).

Show Answer

The density of the neutron star is  $3.4 \times 10^{18} \text{ kg/m}^3$ . The density of a hydrogen nucleus is  $6.0 \times 10^{17} \text{ kg/m}^3$ . The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the **strong nuclear force**. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than  $10^{-15}$  meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

## Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\begin{array}{ccccccc} (2 \times 1.0073 \text{ amu}) & + & (2 \times 1.0087 \text{ amu}) & + & (2 \times 0.00055 \text{ amu}) & = & 4.0331 \text{ amu} \\ \text{protons} & & \text{neutrons} & & \text{electrons} & & \end{array}$$

However, mass spectrometric measurements reveal that the mass of an  ${}^4_2\text{He}$  atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the **mass defect** of the atom. In the case of helium, the mass defect indicates a “loss” in mass of  $4.0331 \text{ amu} - 4.0026 \text{ amu} = 0.0305 \text{ amu}$ . The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The **nuclear binding energy** is the energy produced when the atoms’

nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the **mass-energy equivalence equation** as stated by Albert Einstein:

$$E = mc^2$$

where  $E$  is energy,  $m$  is mass of the matter being converted, and  $c$  is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its mass defect, as demonstrated in Example 2. A variety of units are commonly used for nuclear binding energies, including **electron volts (eV)**, with 1 eV equaling the amount of energy necessary to move the charge of an electron across an electric potential difference of 1 volt, making  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ .

### *Example 2: Calculation of Nuclear Binding Energy*

Determine the binding energy for the nuclide  ${}_2^4\text{He}$  in:

1. joules per mole of nuclei
2. joules per nucleus
3. MeV per nucleus

Show Answer

The mass defect for a  ${}_2^4\text{He}$  nucleus is 0.0305 amu, as

shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ ).

1. First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ . Converting grams into kilograms yields a mass defect of  $3.05 \times 10^{-5} \text{ kg/mol}$ . Substituting this quantity into the mass-energy equivalence equation yields:

$$\begin{aligned} E = mc^2 &= \frac{3.05 \times 10^{-5} \text{ kg}}{\text{mol}} \times \left( \frac{2.998 \times 10^8 \text{ m}}{\text{s}} \right)^2 = 2.74 \times 10^{12} \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \\ &= 2.74 \times 10^{12} \text{ J mol}^{-1} = 2.74 \text{ TJ mol}^{-1} \end{aligned}$$

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

2. The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$E = 2.74 \times 10^{12} \text{ J mol}^{-1} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ nuclei}} = 4.55 \times 10^{-12} \text{ J} = 4.55 \text{ pJ}$$

3. Recall that  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ . Using the binding energy computed in part 2:



$$E = 4.55 \times 10^{-12} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 2.84 \times 10^7 \text{ eV} = 28.4 \text{ MeV}$$

### *Check Your Learning*

What is the binding energy for the nuclide  ${}_{9}^{19}\text{F}$  (atomic mass: 18.9984 amu) in MeV per nucleus?

Show Answer

148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range ( $10^{-9}$  g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range ( $10^{-3}$  g).

## Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This

region is known as the **band of stability** (also called the belt, zone, or valley of stability). The straight line in Figure 1 represents nuclei that have a 1:1 ratio of protons to neutrons ( $n:p$  ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an  $n:p$  ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an  $n:p$  ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

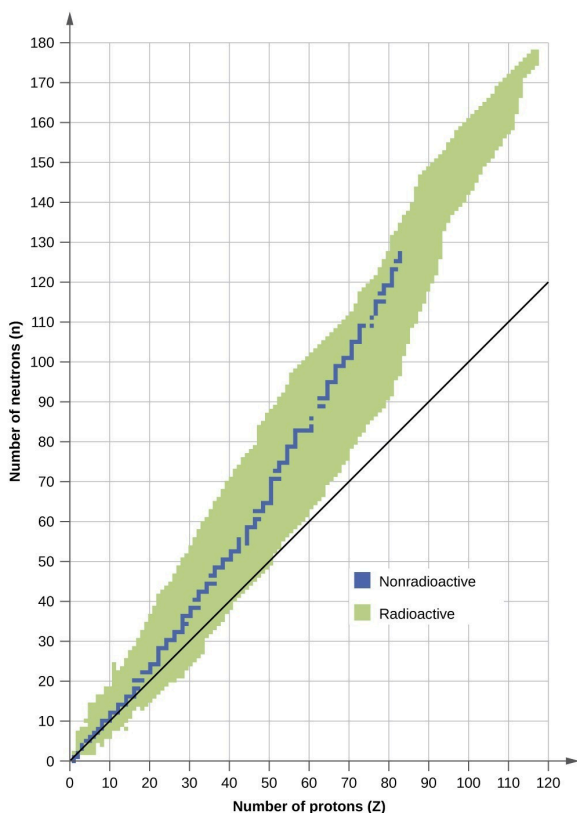


Figure 1. This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where  $n = Z$ .

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit **radioactivity**. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or **radioisotope**) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (see Table 1). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as  ${}^4_2\text{He}$ ,  ${}^{16}_8\text{O}$ ,  ${}^{40}_{20}\text{Ca}$ , and  ${}^{208}_{182}\text{Pb}$ , are called “double magic” and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

**Table 1. Stable Nuclear Isotopes**

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

The relative stability of a nucleus is correlated with its **binding energy per nucleon**, the total binding energy for the nucleus divided by the number of nucleons in the nucleus. For instance, we saw in Example 2 that the binding energy for a  ${}^4_2\text{He}$  nucleus is 28.4 MeV. The binding energy *per nucleon* for a  ${}^4_2\text{He}$  nucleus is therefore:

$$\frac{28.4 \text{ MeV}}{4 \text{ nucleons}} = 7.10 \text{ MeV/nucleon}$$

In Example 3, we learn how to calculate the binding energy per nucleon of a nuclide on the curve shown in Figure 2.

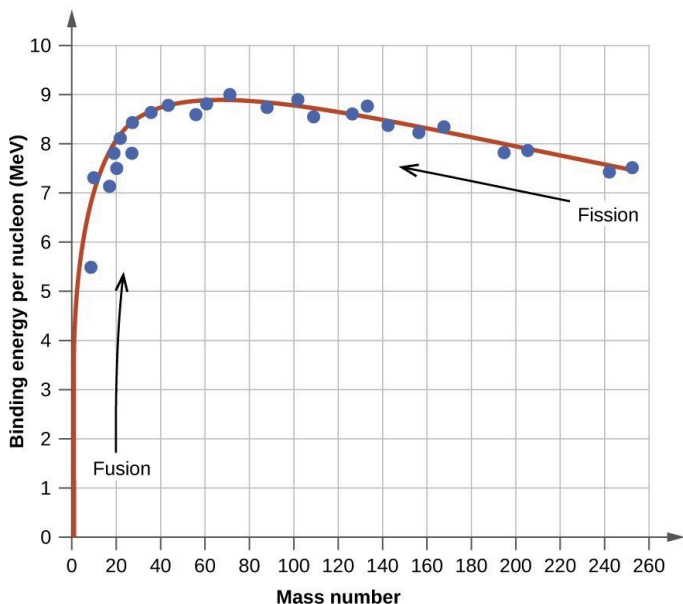


Figure 2. The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

### Example 3: Calculation of Binding Energy per Nucleon

The iron nuclide  $^{56}_{26}\text{Fe}$  lies near the top of the binding energy curve and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide  $^{56}_{26}\text{Fe}$  (atomic mass of 55.9349 amu)?

Show Answer

As in Example 2, we first determine the mass defect of

the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an  $^{56}_{26}\text{Fe}$  atom:

$$\begin{aligned}\text{Mass defect} &= [(26 \times 1.0073 \text{ amu}) + (30 \times 1.0087 \text{ amu}) + (26 \times 0.00055 \text{ amu})] - 55.9349 \text{ amu} \\ &= 56.4651 \text{ amu} - 55.9349 \text{ amu} \\ &= 0.5302 \text{ amu}\end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$\begin{aligned}E = mc^2 &= 0.5302 \text{ amu} \times \frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \times (2.998 \times 10^8 \text{ m/s})^2 \\ &= 7.913 \times 10^{-11} \text{ kg} \cdot \text{m/s}^2 \\ &= 7.913 \times 10^{-11} \text{ J}\end{aligned}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913 \times 10^{-11} \text{ J} \times \frac{1 \text{ MeV}}{1.602 \times 10^{-13} \text{ J}} = 493.9 \text{ MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

$$\text{Binding energy per nucleon} = \frac{493.9 \text{ MeV}}{56} = 8.820 \text{ MeV/nucleon}$$

Note that this is almost 25% larger than the binding energy per nucleon for  $^4_2\text{He}$ .

(Note also that this is the same process as in Example 1, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

### *Check Your Learning*

What is the binding energy per nucleon in  ${}^{19}_9\text{F}$  (atomic mass, 18.9984 amu)?

Show Answer

7.810 MeV/nucleon

### *Key Concepts and Summary*

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This “missing” mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein’s mass-energy equivalence equation,  $E = mc^2$ . Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

## Key Equations

- $E = mc^2$

## Exercises

- Write the following isotopes in hyphenated form (e.g., carbon-14)

- ${}^{24}_{11}\text{Na}$
- ${}^{29}_{13}\text{Al}$
- ${}^{73}_{36}\text{Kr}$
- ${}^{194}_{177}\text{Ir}$

- Write the following isotopes in nuclide notation (e.g.,  ${}^{14}_{16}\text{C}$ )

- oxygen-14
- copper-70
- tantalum-175
- francium-217

- For the following isotopes that have missing information, fill in the missing information to complete the notation

- ${}^{34}_{14}\text{X}$



- b.  $^{36}_{\text{X}}\text{P}$
- c.  $^{57}_{\text{X}}\text{Mn}$
- d.  $^{121}_{56}\text{X}$

4. For each of the isotopes in Question 1, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.
5. Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:
  - a. 25 protons, 20 neutrons, 24 electrons
  - b. 45 protons, 24 neutrons, 43 electrons
  - c. 53 protons, 89 neutrons, 54 electrons
  - d. 97 protons, 146 neutrons, 97 electrons
6. Calculate the density of the  $^{24}_{12}\text{Mg}$  nucleus in g/mL, assuming that it has the typical nuclear diameter of  $1 \times 10^{-13}$  cm and is spherical in shape.
7. What are the two principal differences between nuclear reactions and ordinary chemical changes?
8. The mass of the atom  $^{23}_{11}\text{Na}$  is 22.9898 amu.
  - a. Calculate its binding energy per atom in millions of electron volts.
  - b. Calculate its binding energy per nucleon.
9. Which of the following nuclei lie within the band of stability shown in Figure 1?
  - a. chlorine-37
  - b. calcium-40
  - c.  $^{204}\text{Bi}$
  - d.  $^{56}\text{Fe}$

- e.  $^{206}\text{Pb}$
- f.  $^{211}\text{Pb}$
- g.  $^{222}\text{Rn}$
- h. carbon-14

10. Which of the following nuclei lie within the band of stability shown in Figure 1?

- a. argon-40
- b. oxygen-16
- c.  $^{122}\text{Ba}$
- d.  $^{58}\text{Ni}$
- e.  $^{205}\text{Tl}$
- f.  $^{210}\text{Tl}$
- g.  $^{226}\text{Ra}$
- h. magnesium-24

Show Selected Answers

1. The hyphenated form of each isotope is as follows:

- a. sodium-24
- b. aluminum-29
- c. krypton-73
- d. iridium-194

3. The complete formulas are as follows:

- a.  $^{34}_{14}\text{Si}$
- b.  $^{36}_{15}\text{P}$
- c.  $^{57}_{25}\text{Mn}$
- d.  $^{121}_{56}\text{Ba}$

5. The nuclide notation is as follows:

- a.  ${}_{25}^{45}\text{Mn}^{+1}$
- b.  ${}_{45}^{69}\text{Rh}^{+2}$
- c.  ${}_{53}^{142}\text{I}^{-1}$
- d.  ${}_{97}^{243}\text{Bk}$

7. Nuclear reactions usually change one type of nucleus into another; chemical changes rearrange atoms. Nuclear reactions involve much larger energies than chemical reactions and have measurable mass changes.

9. (a), (b), (c), (d), and (e) all fall within the band of stability shown in Figure 1.

## Glossary

**band of stability:** (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

**binding energy per nucleon:** total binding energy for the nucleus divided by the number of nucleons in the nucleus

**electron volt (eV):** measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

**magic number:** nuclei with specific numbers of nucleons that are within the band of stability

**mass defect:** difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

**mass-energy equivalence equation:** Albert Einstein’s relationship showing that mass and energy are equivalent

**nuclear binding energy:** energy lost when an atom's nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

**nuclear chemistry:** study of the structure of atomic nuclei and processes that change nuclear structure

**nucleon:** collective term for protons and neutrons in a nucleus

**nuclide:** nucleus of a particular isotope

**radioactivity:** phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

**radioisotope:** isotope that is unstable and undergoes conversion into a different, more stable isotope

**strong nuclear force:** force of attraction between nucleons that holds a nucleus together

# 45. Nuclear Equations

## *Learning Objectives*

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

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations







Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are **nuclear reactions**. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

## Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Table 1. Protons ( ${}^1_1\text{p}$ , also represented by the symbol  ${}^1_1\text{H}$ ) and neutrons ( ${}^1_0\text{n}$ ) are the constituents of atomic nuclei, and have been described previously. **Alpha particles** ( ${}^4_2\text{He}$ , also represented by the symbol  ${}^4_2\alpha$ ) are high-energy helium nuclei. **Beta particles** ( ${}^0_{-1}\beta$ , also represented by the symbol  ${}^0_{-1}\text{e}$ ) are

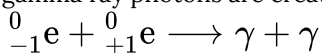
high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. **Positrons** ( ${}^0_{+1}\beta$ , also represented by the symbol  ${}^0_{+1}\beta$ ) are positively charged electrons (“anti-electrons”). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized  ${}^4_2\text{He}$ . This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Although many species are encountered in nuclear reactions, Table 1 summarizes the names, symbols, representations, and descriptions of the most common of these.

Table 1. Nuclear Particles			
Name	Symbol(s)	Representation	Description
Alpha particle	${}^4_2\text{He}$ or ${}^4_2\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	${}^0_{-1}\text{e}$ or ${}^0_{-1}\beta$		(High-energy) electrons
Positron	${}^0_{+1}\text{e}$ or ${}^0_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	${}^1_1\text{H}$ or ${}^1_1\text{p}$		Nuclei of hydrogen atoms
Neutron	${}^1_0\text{n}$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	$\gamma$		Very high-energy electromagnetic radiation

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of **antimatter**, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of **gamma rays ( $\gamma$ )**—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy

equivalence equation  $E = mc^2$ , seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:



As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

## Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the



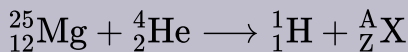
particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that  ${}^{17}_8\text{O}$  is a product of the nuclear reaction of  ${}^{14}_7\text{N}$  and  ${}^4_2\text{He}$  if we knew that a proton,  ${}^1_1\text{H}$ , was one of the two products. Example 1 shows how we can identify a nuclide by balancing the nuclear reaction.

### *Example 1: Balancing Equations for Nuclear Reactions*

The reaction of an  $\alpha$  particle with magnesium-25 ( ${}^{25}_{12}\text{Mg}$ ) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Show Answer

The nuclear reaction can be written as:



where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = A + 1, \text{ or } A = 28$$

Similarly, the charges must balance, so:

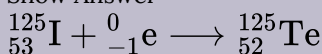
$$12 + 2 = Z + 1, \text{ and } Z = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is  ${}^{28}_{13}\text{Al}$ .

### Check Your Learning

The nuclide  $^{125}_{53}\text{I}$  combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Show Answer



Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie **Curie** and her husband Pierre in 1898. It decays, emitting  $\alpha$  particles:
  - $^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^4_2\text{He}$
- The first nuclide to be prepared by artificial means was an isotope of oxygen,  $^{17}\text{O}$ . It was made by Ernest **Rutherford** in 1919 by bombarding nitrogen atoms with  $\alpha$  particles:
  - $^{14}_7\text{N} + {}^4_2\alpha \longrightarrow {}^{17}_8\text{O} + {}^1_1\text{H}$
- James **Chadwick** discovered the neutron in 1932, as a previously unknown neutral particle produced along with  $^{12}\text{C}$  by the nuclear reaction between  $^9\text{Be}$  and  $^4\text{He}$ :
  - $^9_4\text{Be} + {}^4_2\text{He} \longrightarrow {}^{12}_6\text{C} + {}^1_0\text{n}$
- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen,  $^2_1\text{H}$ ), by Emilio **Segre** and Carlo **Perrier** in 1937:

- ${}^2_1\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^1_0\text{n} + {}^{97}_{43}\text{Tc}$
- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:
  - ${}^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^1_0\text{n}$

### *Key Concepts and Summary*

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha ( $\alpha$ ) particles (which are high-energy helium nuclei), beta ( $\beta$ ) particles (which are high-energy electrons), and gamma ( $\gamma$ ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

### *Exercises*

Write a brief description or definition of each of the following:

1. nucleon
2.  $\alpha$  particle

3.  $\beta$  particle
4. positron
5.  $\gamma$  ray
6. nuclide
7. mass number
8. atomic number

Show Answer

1. A nucleon is any particle contained in the nucleus of the atom, so it can refer to protons and neutrons.
2. An  $\alpha$  particle is one product of natural radioactivity and is the nucleus of a helium atom.
3. A  $\beta$  particle is a product of natural radioactivity and is a high-speed electron.
4. A positron is a particle with the same mass as an electron but with a positive charge.
5. Gamma rays compose electromagnetic radiation of high energy and short wavelength.
6. Nuclide is a term used when referring to a single type of nucleus.
7. The mass number is the sum of the number of protons and the number of neutrons in an element.
8. The atomic number is the number of protons in the nucleus of an element.

## Exercises

- Which of the various particles ( $\alpha$  particles,  $\beta$  particles, and so on) that may be produced in a nuclear reaction are actually nuclei.
- Complete each of the following equations by adding the missing species:

- ${}_{13}^{27}\text{Al} + {}_2^4\text{He} \longrightarrow ? + {}_0^1\text{n}$
- ${}_{94}^{239}\text{Pu} + ? \longrightarrow {}_{96}^{242}\text{Cm} + {}_0^1\text{n}$
- ${}_{7}^{14}\text{N} + {}_2^4\text{He} \longrightarrow ? + {}_1^1\text{H}$
- ${}_{92}^{235}\text{U} \longrightarrow ? + {}_{55}^{135}\text{Cs} + 4{}_0^1\text{n}$

- Complete each of the following equations:

- ${}_3^7\text{Li} + ? \longrightarrow 2{}_2^4\text{He}$
- ${}_6^{14}\text{C} \longrightarrow {}_7^{14}\text{N} + ?$
- ${}_{13}^{27}\text{Al} + {}_2^4\text{He} \longrightarrow ? + {}_0^1\text{n}$
- ${}_{96}^{250}\text{Cm} \longrightarrow ? + {}_{38}^{98}\text{Sr} + 4{}_0^1\text{n}$

- Write a balanced equation for each of the following nuclear reactions:

- the production of  ${}^{17}\text{O}$  from  ${}^{14}\text{N}$  by  $\alpha$  particle bombardment
- the production of  ${}^{14}\text{C}$  from  ${}^{14}\text{N}$  by neutron bombardment
- the production of  ${}^{233}\text{Th}$  from  ${}^{232}\text{Th}$  by neutron bombardment
- the production of  ${}^{239}\text{U}$  from  ${}^{238}\text{U}$  by  ${}_1^2\text{H}$  bombardment

5. Technetium-99 is prepared from  $^{98}\text{Mo}$ . Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a  $\beta$  particle to yield an excited form of technetium-99, represented as  $^{99}\text{Tc}^*$ . This excited nucleus relaxes to the ground state, represented as  $^{99}\text{Tc}$ , by emitting a  $\gamma$  ray. The ground state of  $^{99}\text{Tc}$  then emits a  $\beta$  particle. Write the equations for each of these nuclear reactions.
6. The mass of the atom  $^{19}_9\text{F}$  is 18.99840 amu.
- Calculate its binding energy per atom in millions of electron volts.
  - Calculate its binding energy per nucleon.
7. For the reaction  $^{14}_6\text{C} \longrightarrow ^{14}_7\text{N} + ?$ , if 100.0 g of carbon reacts, what volume of nitrogen gas ( $\text{N}_2$ ) is produced at 273K and 1 atm?

Show Selected Answers

2. The completed equations are as follows:

- $^{27}_{13}\text{Al} + ^4_2\text{He} \longrightarrow ^{30}_{15}\text{P} + ^1_0\text{n}$
- $^{239}_{94}\text{Pu} + ^4_2\text{He} \longrightarrow ^{242}_{96}\text{Cm} + ^1_0\text{n}$
- $^{14}_7\text{N} + ^4_2\text{He} \longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$
- $^{235}_{92}\text{U} \longrightarrow ^{96}_{37}\text{Rb} + ^{135}_{55}\text{Cs} + 4^1_0\text{n}$

4. The balanced equations are as follows:

- $^{14}_7\text{N} + ^4_2\text{He} \longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$
- $^{14}_7\text{N} + ^1_0\text{n} \longrightarrow ^{14}_6\text{N} + ^1_1\text{H}$
- $^{232}_{90}\text{Th} + ^1_0\text{n} \longrightarrow ^{233}_{90}\text{Th}$
- $^{238}_{92}\text{U} + ^1_1\text{H} \longrightarrow ^{239}_{92}\text{U} + ^1_1\text{H}$

6. The answers are as follows:

- a. Determine the mass defect of the nuclide, which is the difference between the mass of 9 protons, 10 neutrons, and 9 electrons, and the observed mass of a  ${}^{19}_{9}\text{F}$  atom:

$$\begin{aligned}\text{mass defect} &= [(9 \times 1.0073 \text{ amu}) + (10 \times 1.0087 \text{ amu}) + (9 \times 0.00055 \text{ amu})] - 18.99840 \text{ amu} \\ &= 19.15765 \text{ amu} - 18.99840 \text{ amu} \\ &= 0.15925 \text{ amu}\end{aligned}$$

$$\begin{aligned}E = mc^2 &= 0.15925 \text{ amu} \times \frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \times \left(2.998 \times 10^8 \frac{\text{m}}{\text{s}}\right)^2 \\ &= 2.377 \times 10^{-11} \text{ kg m}^2/\text{s}^2 \\ &= 2.377 \times 10^{-11} \text{ J}\end{aligned}$$

$$2.377 \times 10^{-11} \text{ J} \times \frac{1 \text{ MeV}}{1.602 \times 10^{-13} \text{ J}} = 148.8 \text{ MeV per atom}$$

- b. Binding energy per nucleon =

$$\frac{148.4 \text{ MeV}}{19} = 7.808 \text{ MeV/nucleon}$$

## Glossary

**alpha particle:** ( $\alpha$  or  ${}^4_2\text{He}$  or  ${}^4_2\alpha$ ) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

**antimatter:** particles with the same mass but opposite properties (such as charge) of ordinary particles

**beta particle:**  $\beta$  or  ${}^0_{-1}\text{e}$  or  ${}^0_{-1}\beta$ ) high-energy electron

**gamma ray:** ( $\gamma$  or  ${}^0_0\gamma$ ) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

**nuclear reaction:** change to a nucleus resulting in changes in the atomic number, mass number, or energy state

**positron** ( ${}^0_{+1}\beta$  or  ${}^0_{+1}\text{e}$ ) : antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge



## 46. Radioactive Decay

### *Learning Objectives*

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

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term “radioactivity,” and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is **radioactive decay**. The unstable nuclide is called the **parent nuclide**; the nuclide that results from the decay is known as the **daughter nuclide**. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is

such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo.

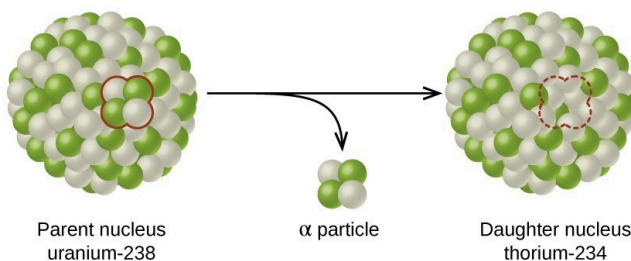


Figure 1. A nucleus of uranium-238 (the parent nuclide) undergoes a decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Watch this video to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.



One or more interactive elements has been excluded from this version of the text. You can view them online here:

[https://library.achievingthedream.org/  
sanjacintroductorychemistry/?p=72#oembed-1](https://library.achievingthedream.org/sanjacintroductorychemistry/?p=72#oembed-1)

## Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field helped him determine that one type of radiation consisted of positively charged and relatively massive  $\alpha$  particles; a second type was made up of negatively charged and much less massive  $\beta$  particles; and a third was uncharged electromagnetic waves,  $\gamma$  rays. We now know that  $\alpha$  particles are high-energy helium nuclei,  $\beta$  particles are high-energy electrons, and  $\gamma$  radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

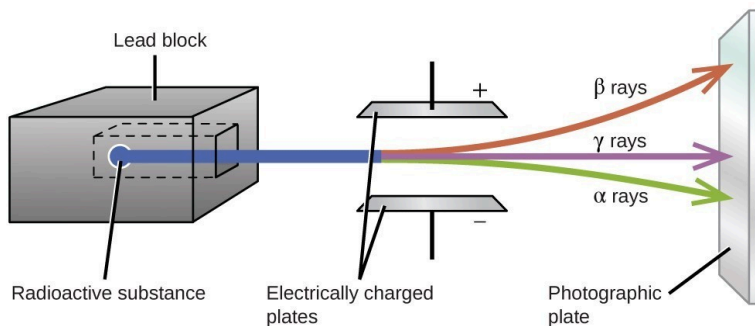
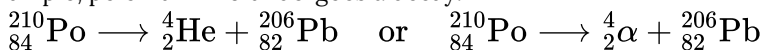


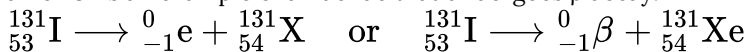
Figure 2. Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

**Alpha ( $\alpha$ ) decay** is the emission of an  $\alpha$  particle from the nucleus. For example, polonium-210 undergoes  $\alpha$  decay:



Alpha decay occurs primarily in heavy nuclei ( $A > 200$ ,  $Z > 83$ ). Because the loss of an  $\alpha$  particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing  $\alpha$  decay lies below the band of stability, the daughter nuclide will lie closer to the band.

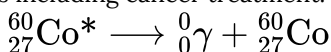
**Beta ( $\beta$ ) decay** is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes  $\beta$  decay:



Beta decay, which can be thought of as the conversion of a neutron into a proton and a  $\beta$  particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of

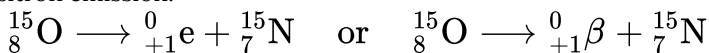
an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

**Gamma emission ( $\gamma$  emission)** is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a  $\gamma$  ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (\*). Cobalt-60 emits  $\gamma$  radiation and is used in many applications including cancer treatment:



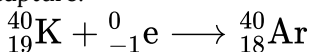
There is no change in mass number or atomic number during the emission of a  $\gamma$  ray unless the  $\gamma$  emission accompanies one of the other modes of decay.

**Positron emission ( $\beta^+$  decay)** is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:



Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

**Electron capture** occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:



Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture

has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

Figure 3 summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

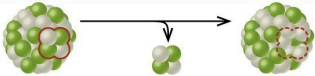
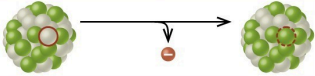
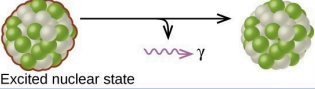
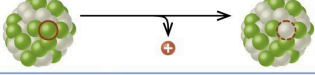
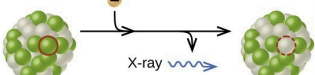
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^A_ZX \rightarrow {}^4_2\text{He} + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^A_ZX \rightarrow {}^0_{-1}e + {}^A_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^A_ZX \rightarrow {}^0_0\gamma + {}^A_ZY$		A: unchanged Z: unchanged
Positron emission	${}^A_ZX \rightarrow {}^0_{+1}e + {}^A_{Z-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^A_ZX + {}^0_{-1}e \rightarrow {}^A_{Z-1}Y + \nu$		A: unchanged Z: decrease by 1

Figure 3. This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

## PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient's body function (Figure 4). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This “tagged” compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

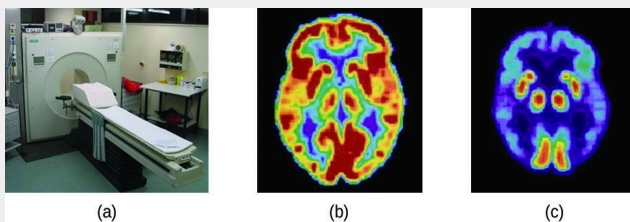


Figure 4. A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

For example, F-18 is produced by proton bombardment of  $^{18}\text{O}$  ( $^{18}_8\text{O} + {}^1_1\text{p} \longrightarrow {}^{18}_9\text{F} + {}^1_0\text{n}$ )

and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The  $^{18}\text{F}$  emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

## Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or **radioactive decay series**. Three of these series include most of the naturally radioactive elements of the periodic table. They are the



uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure 5). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

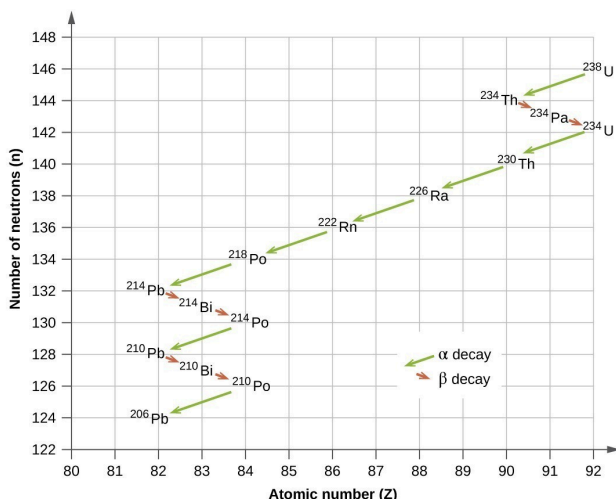


Figure 5. Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight  $\alpha$  decays and six  $\beta$  decays.

## Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ( $t_{1/2}$ ),

the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure 6). In a given cobalt-60 source, since half of the  $^{60}_{27}\text{Co}$  nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

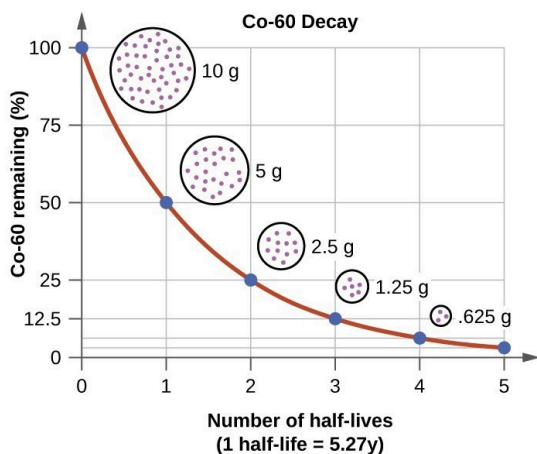


Figure 6. For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions.

We generally substitute the number of nuclei,  $N$ , for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the activity of the radioactive sample. The rate for radioactive decay is:

decay rate =  $\lambda N$  with  $\lambda$  = the decay constant for the particular radioisotope

The decay constant,  $\lambda$ , which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life,  $t_{1/2}$ :

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \quad \text{or} \quad t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount,  $N$ , and time are:

$$N_t = N_0 e^{-kt} \quad \text{or} \quad t = -\frac{1}{\lambda} \ln \left( \frac{N_t}{N_0} \right)$$

where  $N_0$  is the initial number of nuclei or moles of the isotope, and  $N_t$  is the number of nuclei/moles remaining at time  $t$ . Example 1 applies these calculations to find the rates of radioactive decay for specific nuclides.

### *Example 1: Rates of Radioactive Decay*

$^{60}_{27}\text{Co}$  decays with a half-life of 5.27 years to produce  $^{60}_{28}\text{Ni}$ .

1. What is the decay constant for the radioactive disintegration of cobalt-60?
2. Calculate the fraction of a sample of the  $^{60}_{27}\text{Co}$  isotope that will remain after 15 years.
3. How long does it take for a sample of  $^{60}_{27}\text{Co}$  to disintegrate to the extent that only 2.0% of the

original amount remains?

Show Answer

1. The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27\text{y}} = 0.132\text{y}^{-1}$$

2. The fraction of  $^{60}_{27}\text{Co}$  that is left after time  $t$  is

given by  $\frac{N_t}{N_0}$ . Rearranging the first-order

relationship  $N_t = N_0 e^{-\lambda t}$  to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15.0/\text{y})} = 0.138$$

The fraction of  $^{60}_{27}\text{Co}$  that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the  $^{60}_{27}\text{Co}$  originally present will remain after 15 years.

3. 2.00% of the original amount of  $^{60}_{27}\text{Co}$  is equal to  $0.0200 \times N_0$ . Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda} \ln \left( \frac{N_t}{N_0} \right) = -\frac{1}{0.132\text{y}^{-1}} \ln \left( \frac{0.0200 \times N_0}{N_0} \right) = 29.6\text{y}$$

### Check Your Learning

Radon-222,  $^{222}_{86}\text{Rn}$ , has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Show Answer

11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of  $^{209}_{83}\text{Bi}$  is  $1.9 \times 10^{19}$  years;  $^{239}_{94}\text{Ra}$  is 24,000 years;  $^{222}_{86}\text{Rn}$  is 3.82 days; and element-111 (Rg for roentgenium) is  $1.5 \times 10^{-3}$  seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table 1, and others are listed in [Half-Lives for Several Radioactive Isotopes](#).

Table 1. Half-lives of Radioactive Isotopes Important to Medicine			
Type <sup>1</sup>	Decay Mode	Half-Life	Uses
F-18	$\beta^+$ decay	110. minutes	PET scans
Co-60	$\beta$ decay, $\gamma$ decay	5.27 years	cancer treatment
Tc-99m	$\gamma$ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	$\beta$ decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

## Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of “dating” the origin of objects such as archaeological artifacts, formerly living organisms, or geological

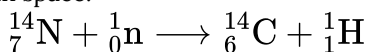
1. The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit  $\gamma$  radiation to rid themselves of excess energy and become (more) stable.

formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

## Radioactive Dating Using Carbon-14

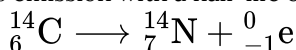
The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes:  ${}^{12}_6\text{C}$ , which constitutes about 99% of the carbon on earth;  ${}^{13}_6\text{C}$ , about 1% of the total; and trace amounts of  ${}^{14}_6\text{C}$ . Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:



All isotopes of carbon react with oxygen to produce  $\text{CO}_2$  molecules. The ratio of  ${}^{14}_6\text{CO}_2$  to  ${}^{12}_6\text{CO}_2$  depends on the ratio of  ${}^{14}_6\text{CO}$  to  ${}^{12}_6\text{CO}$  in the atmosphere. The natural abundance of  ${}^{14}_6\text{CO}$  in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen in gas samples found trapped in ice. The incorporation of  ${}^{14}_6\text{CO}_2$  and  ${}^{12}_6\text{CO}_2$  into plants is a regular part of the photosynthesis process, which means that the  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  ratio found in a living plant is the same as the  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because  ${}^{12}_6\text{C}$  is a stable isotope and does not undergo radioactive

decay, its concentration in the plant does not change. However, carbon-14 decays by  $\beta$  emission with a half-life of 5730 years:



Thus, the  ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$  ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure 7 visually depicts this process.

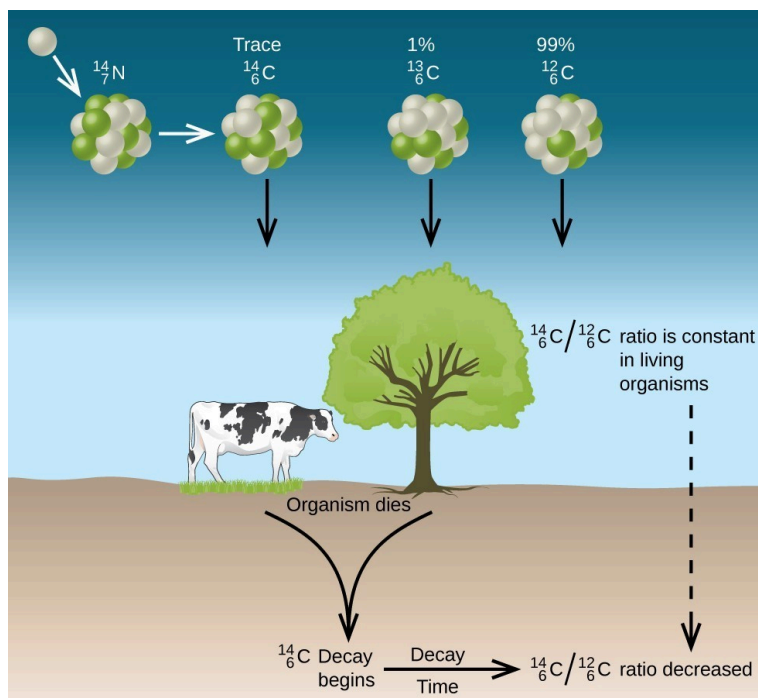


Figure 7. Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of  ${}^{14}_{6}\text{C}$  being 5730 years, if the  ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$  ratio in a wooden object found in an archaeological dig

is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

[Visit this website to perform simulations of radiometric dating.](#)

### Example 2: Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Show Answer

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts,  $N$ , in the relationship:

$$t = -\frac{1}{\lambda} \ln \left( \frac{N_t}{N_0} \right) \longrightarrow t = -\frac{1}{\lambda} \ln \left( \frac{\text{Rate}_t}{\text{Rate}_0} \right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript  $t$  represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:



$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730 \text{ y}} = 1.21 \times 10^{-4} \text{ y}^{-1}.$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda} \ln \left( \frac{\text{Rate}_t}{\text{Rate}_0} \right) = -\frac{1}{1.21 \times 10^{-4} \text{ y}^{-1}} \ln \left( \frac{10.8 \text{ dis/min/g C}}{13.6 \text{ dis/min/g C}} \right) = 1910 \text{ y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 8).



Figure 8. Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BCE and CE 50.

### Check Your Learning

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Show Answer

about 3350 years ago, or approximately 1340 BCE

There have been some significant, well-documented changes to the  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  ratio. The accuracy of a straightforward application of this technique depends on the  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of  $\text{CO}_2$  molecules (largely  ${}^{12}_6\text{CO}_2$ ) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the  ${}^{14}_6\text{C}$  has decayed), the ratio of  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  in the atmosphere may be changing. This manmade increase in  ${}^{12}_6\text{CO}_2$  in the atmosphere causes the  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

## Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there

is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

### *Example 3: Radioactive Dating of Rocks*

An igneous rock contains  $9.58 \times 10^{-5}$  g of U-238 and  $2.51 \times 10^{-5}$  g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Show Answer

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5} \cancel{\text{g U}} \times \left( \frac{1 \text{ mol U}}{238 \cancel{\text{g U}}} \right) = 4.03 \times 10^{-7} \text{ mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5} \cancel{\text{g Pb}} \times \left( \frac{1 \cancel{\text{mol Pb}}}{206 \cancel{\text{g Pb}}} \right) \times \left( \frac{1 \text{ mol U}}{1 \cancel{\text{mol Pb}}} \right) = 1.22 \times 10^{-7} \text{ mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7} \text{ mol} + 1.22 \times 10^{-7} \text{ mol} = 5.25 \times 10^{-7} \text{ mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda} \ln \left( \frac{N_t}{N_0} \right)$$

with  $N_0$  representing the original amount of U-238 and  $N_t$  representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of  $4.5 \times 10^9$  y, so the decay constant  $\lambda$  is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ y}} = 1.54 \times 10^{-10} \text{ y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10} \text{ y}^{-1}} \ln \left( \frac{4.03 \times 10^{-7} \cancel{\text{mol U}}}{5.25 \times 10^{-7} \cancel{\text{mol U}}} \right) = 1.7 \times 10^9 \text{ y}$$

Therefore, the rock is approximately 1.7 billion years old.

### *Check Your Learning*

A sample of rock contains  $6.14 \times 10^{-4}$  g of Rb-87 and  $3.51 \times 10^{-5}$  g of Sr-87. Calculate the age of the rock. (The half-life of the  $\beta$  decay of Rb-87 is  $4.7 \times 10^{10}$  y.)

Show Answer

$3.7 \times 10^9$  y

### *Key Concepts and Summary*

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are  $\alpha$  decay,  $\beta$  decay,  $\gamma$  emission, positron emission, and electron capture. Nuclear reactions also often involve  $\gamma$  rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in

medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

### *Key Equations*

- decay rate =  $\lambda N$
- $t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$

### *Exercises*

1. What are the types of radiation emitted by the nuclei of radioactive elements?
2. What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?
  - a. an  $\alpha$  particle is emitted
  - b. a  $\beta$  particle is emitted
  - c.  $\gamma$  radiation is emitted
  - d. a positron is emitted
  - e. an electron is captured
3. What is the change in the nucleus that results from the following decay scenarios?
  - a. emission of a  $\beta$  particle
  - b. emission of a  $\beta^+$  particle

- c. capture of an electron
4. Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include  $\alpha$  particles.
5. Why is electron capture accompanied by the emission of an X-ray?
6. Explain how unstable heavy nuclides (atomic number  $> 83$ ) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.
7. Which of the following nuclei is most likely to decay by positron emission? Explain your choice.
  - a. chromium-53
  - b. manganese-51
  - c. iron-59
8. The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.
  - a.  $^{34}_{15}\text{P}$
  - b.  $^{239}_{92}\text{U}$
  - c.  $^{38}_{20}\text{Ca}$
  - d.  $^3_1\text{H}$
  - e.  $^{245}_{94}\text{Pu}$
9. The following nuclei do not lie in the band of stability. How would they be expected to decay?
  - a.  $^{28}_{15}\text{P}$

- b.  ${}_{92}^{235}\text{U}$
- c.  ${}_{20}^{37}\text{Ca}$
- d.  ${}_{3}^9\text{Li}$
- e.  ${}_{96}^{245}\text{Cm}$

10. Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

- a.  ${}_{2}^6\text{He}$
- b.  ${}_{30}^{60}\text{Zn}$
- c.  ${}_{91}^{235}\text{Pa}$
- d.  ${}_{94}^{241}\text{Np}$
- e.  ${}_{18}^9\text{F}$
- f.  ${}_{56}^{129}\text{Ba}$
- g.  ${}_{94}^{237}\text{Pu}$

11. Write a nuclear reaction for each step in the formation of  ${}_{84}^{218}\text{Po}$  from  ${}_{98}^{238}\text{U}$ , which proceeds by a series of decay reactions involving the step-wise emission of  $\alpha$ ,  $\beta$ ,  $\beta$ ,  $\alpha$ ,  $\alpha$ ,  $\alpha$  particles, in that order.
12. Write a nuclear reaction for each step in the formation of  ${}_{82}^{208}\text{Pb}$  from  ${}_{90}^{228}\text{Th}$ , which proceeds by a series of decay reactions involving the step-wise emission of  $\alpha$ ,  $\alpha$ ,  $\alpha$ ,  $\alpha$ ,  $\beta$ ,  $\beta$ ,  $\alpha$  particles, in that order.
13. Define the term half-life and illustrate it with an example.
14. A  $1.00 \times 10^{-6}$ -g sample of nobelium,  ${}_{102}^{254}\text{No}$ , has a half-life of 55 seconds after it is formed. What is the percentage of  ${}_{102}^{254}\text{No}$  remaining at the following times?



- a. 5.0 min after it forms
  - b. 1.0 h after it forms
15.  $^{239}\text{Pu}$  is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the  $^{239}\text{Pu}$  present today will be present in 1000 y?
16. The isotope  $^{208}\text{Tl}$  undergoes  $\beta$  decay with a half-life of 3.1 min.
  - a. What isotope is produced by the decay?
  - b. How long will it take for 99.0% of a sample of pure  $^{208}\text{Tl}$  to decay?
  - c. What percentage of a sample of pure  $^{208}\text{Tl}$  remains un-decayed after 1.0 h?
17. If 1.000 g of  $^{226}_{88}\text{Ra}$  produces 0.0001 mL of the gas  $^{222}_{86}\text{Rn}$  at STP (standard temperature and pressure) in 24 h, what is the half-life of  $^{226}\text{Ra}$  in years?
18. The isotope  $^{90}_{38}\text{Sr}$  is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.
19. Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of  $^{99}_{43}\text{Tc}$ .
20. What is the age of mummified primate skin that contains 8.25% of the original quantity of  $^{14}\text{C}$ ?
21. A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.
  - a. Calculate the age of the rock if the half-life of

the decay of rubidium by  $\beta$  emission is  $4.7 \times 10^{10}$  y.

- b. If some  ${}^{87}_{38}\text{Sr}$  was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.
22. A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of  ${}^{238}_{92}\text{U}$  and 2.52 mg of  ${}^{206}_{82}\text{Pb}$ . Calculate the age of the ore. The half-life of  ${}^{238}_{92}\text{U}$  is  $4.5 \times 10^9$  yr.
23. Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this  ${}^{239}\text{Pu}$  was the capture of neutrons by  ${}^{238}\text{U}$  nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed  $4.7 \times 10^9$  years ago?
24. A  ${}^7_4\text{Be}$  atom (mass = 7.0169 amu) decays into a  ${}^7_3\text{Li}$  atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?
25. A  ${}^8_5\text{B}$  atom (mass = 8.0246 amu) decays into a  ${}^8_4\text{B}$  atom (mass = 8.0053 amu) by loss of a  $\beta^+$  particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?
26. Isotopes such as  ${}^{26}\text{Al}$  (half-life:  $7.2 \times 10^5$  years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

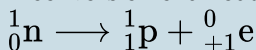
- a.  $^{26}\text{Al}$  decays by  $\beta^+$  emission or electron capture. Write the equations for these two nuclear transformations.
- b. The earth was formed about  $4.7 \times 10^9$  (4.7 billion) years ago. How old was the earth when 99.999999% of the  $^{26}\text{Al}$  originally present had decayed?
27. Write a balanced equation for each of the following nuclear reactions:
- a. bismuth-212 decays into polonium-212
- b. beryllium-8 and a positron are produced by the decay of an unstable nucleus
- c. neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239
- d. strontium-90 decays into yttrium-90
28. Write a balanced equation for each of the following nuclear reactions:
- a. mercury-180 decays into platinum-176
- b. zirconium-90 and an electron are produced by the decay of an unstable nucleus
- c. thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay
- d. neon-19 decays into fluorine-19

Show Answer

1.  $\alpha$  (helium nuclei),  $\beta$  (electrons),  $\beta^+$  (positrons), and  $\eta$  (neutrons) may be emitted from a radioactive element, all of which are particles;  $\gamma$  rays also may be emitted.

3. The changes are as follows:

- a. conversion of a neutron to a proton:



- b. conversion of a proton to a neutron; the positron has the same mass as an electron and the same magnitude of positive charge as the electron has negative charge; when the n:p ratio of a nucleus is too low, a proton is converted into a neutron with the emission of a positron:  ${}_1^1\text{p} \longrightarrow {}_0^1\text{n} + {}_{+1}^0\text{e}$

- c. In a proton-rich nucleus, an inner atomic electron can be absorbed. In simplified form, this changes a proton into a neutron:  ${}_1^1\text{p} + {}_{-1}^0\text{e} \longrightarrow {}_0^1\text{p}$

5. The electron pulled into the nucleus was most likely found in the 1s orbital. As an electron falls from a higher energy level to replace it, the difference in the energy of the replacement electron in its two energy levels is given off as an X-ray.

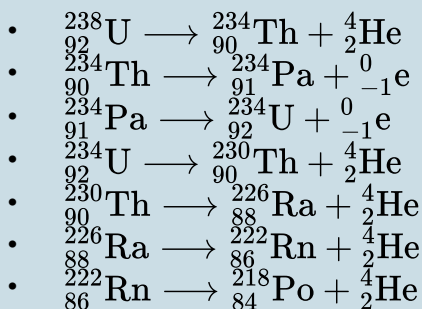
7. Manganese-51 is most likely to decay by positron emission. The n:p ratio for Cr-53 is  $\frac{29}{24} = 1.21$ ; for Mn-51, it is  $\frac{26}{25} = 1.04$ ; for Fe-59, it is  $\frac{33}{26} = 1.27$ . Positron decay occurs when the n:p ratio is low. Mn-51 has the lowest n:p ratio and therefore is most likely to decay by positron emission. Besides,  ${}_{24}^{53}\text{Cr}$  is a stable isotope, and  ${}_{26}^{59}\text{Fe}$  decays by beta emission.

9. The expected decay for each nucleus is as follows:

- a. too many neutrons,  $\beta$  decay  
b. atomic number greater than 82,  $\alpha$  decay

- c. too few neutrons, positron emission
- d. too many neutrons,  $\beta$  decay
- e. atomic number greater than 83,  $\alpha$  decay

11. The reactions are as follows:



13. Half-life is the time required for half the atoms in a sample to decay. Example (answers may vary): For C-14, the half-life is 5770 years. A 10-g sample of C-14 would contain 5 g of C-14 after 5770 years; a 0.20-g sample of C-14 would contain 0.10 g after 5770 years.

15. 1000 years is 0.04 half-lives. The fraction that remains after 0.04 half-lives is  $\left(\frac{1}{2}\right)^{0.04} = 0.973$  or 97.3%

17.  $PV = nRT$

$$\frac{PV}{RT} = \frac{n_{\text{Rn}} (1 \text{ atm}) (0.0001 \text{ mL} \times 1 \text{ L}/10^3 \text{ mL})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (273.15 \text{ K})}$$

$$= 4.4614 \times 10^{-9} \text{ mol}$$

$$n_{\text{Rn}} \text{ produced} = n_{\text{Rn}} \text{ decayed}$$

$$\text{mass Ra lost} = 4.4614 \times 10^{-9} \text{ mol} \times \frac{226 \text{ g}}{\text{mol}} = 1.00827 \times 10^{-6} \text{ g}$$

$$\text{mass Ra remaining after 24 h} = 1 - (1.00827 \times 10^{-6} \text{ g}) = 9.9999899 \times 10^{-1} \text{ g}$$

$$\ln \frac{c_0}{c} = \lambda t = \ln$$

$$\frac{1.000}{9.9999899 \times 10^{-1}} = \lambda (24 \text{ h}) = 4.3785 \times 10^{-7}$$

$$\lambda = 4.2015 \times 10^{-8} \text{ h}^{-1}$$

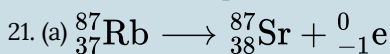
$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{4.2015 \times 10^{-8} \text{ h}^{-1}} = 1.6494 \times 10^7 \text{ h}$$

$$= 1.6494 \times 10^7 \text{ h} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ y}}{365 \text{ d}} = 1.883 \times 10^3 \text{ y}$$

or  $2 \times 10^3 \text{ y}$

19. (Recall that radioactive decay is a first-order process.)

$$\lambda = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{6.0 \text{ h}} = 0.12 \text{ h}^{-1}$$



${}^{87}_{38}\text{Sr}$  is a stable isotope and does not decay further.

Calculate the value of the decay rate constant for  ${}^{87}_{37}\text{Rb}$ , remembering that all radioactive decay is first order:

$$\lambda = \frac{0.693}{4.7 \times 10^{10} \text{ y}} = 1.47 \times 10^{-11} \text{ y}^{-1}$$

Calculate the number of moles of  ${}^{87}_{37}\text{Rb}$  and  ${}^{87}_{38}\text{Sr}$  found in the sample at time  $t$ :

$$8.23\text{mg} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mol}}{87.0\text{g}} = 9.46 \times 10^{-5}\text{mol of } {}^{87}_{37}\text{Rb}$$

$$0.47\text{mg} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mol}}{87.0\text{g}} = 5.40 \times 10^{-6}\text{mol of } {}^{87}_{38}\text{Sr}$$

Each mol of  ${}^{87}_{37}\text{Rb}$  that disappeared (by radioactive decay of the  ${}^{87}_{37}\text{Rb}$  initially present in the rock) produced 1 mol of  ${}^{87}_{38}\text{Sr}$ . Hence the number of moles of  ${}^{87}_{38}\text{Rb}$  that disappeared by radioactive decay equals the number of moles of  ${}^{87}_{38}\text{Sr}$  that were produced. This amount consists of the  $5.40 \times 10^{-6}\text{ mol}$  of  ${}^{87}_{38}\text{Sr}$  found in the rock at time  $t$  if all the  ${}^{87}_{38}\text{Sr}$  present at time  $t$  resulted from radioactive decay of  ${}^{87}_{37}\text{Rb}$  and no strontium-87 was present initially in the rock. Using this assumption, we can calculate the total number of moles of rubidium-87 initially present in the rock:

Total number of moles of  ${}^{87}_{37}\text{Rb}$  initially present in the rock at time  $t = 0$  = number of moles of  ${}^{87}_{37}\text{Rb}$  at time  $t$  + number of moles of  ${}^{87}_{37}\text{Rb}$  that decayed during the time interval  $t - t_0$  = number of moles of  ${}^{87}_{37}\text{Rb}$  measured at time  $t$  + number of moles of  ${}^{87}_{38}\text{Sr}$  measured at time  $t = 9.46 \times 10^{-5}\text{ mol} + 5.40 \times 10^{-6}\text{ mol} = 1.00 \times 10^{-4}\text{ mol}$

The number of moles can be substituted for concentrations in the expression:

$$\ln \frac{c_0}{c_t} = \lambda t$$

Thus:

$$\ln \frac{1.00 \times 10^{-4}\text{mol}}{9.46 \times 10^{-5}\text{mol}} = (1.47 \times 10^{-11})t$$

$$t = \left( \ln \frac{1.00 \times 10^{-4}}{9.46 \times 10^{-5}} \right) \left( \frac{1}{1.47 \times 10^{-11}\text{y}^{-1}} \right)$$

$$= 3.8 \times 10^9 \text{ y} = 3.8 \text{ billion years} = \text{age of the rock sample}$$

(b) The rock would be younger than the age calculated in part (a). If Sr was originally in the rock, the amount produced by radioactive decay would equal the present amount minus the initial amount. As this amount would be smaller than the amount used to calculate the age of the rock and the age is proportional to the amount of Sr, the rock would be younger.

23.  ${}_{94}^{239}\text{Pu}$  has a half-life of  $2.411 \times 10^4 \text{ y}$ . Calculate the value of  $\lambda$  and then determine the amount of plutonium-239 remaining after  $4.7 \times 10^9 \text{ y}$ :

$$\lambda t = \lambda(2.411 \times 10^4 \text{ y}) = \ln \left( \frac{1.0000}{0.5000} \right) = 0.6931$$

$$\lambda = \frac{0.6931}{2.411} \times 10^4 \text{ y} = 2.875 \times 10^{-5} \text{ y}^{-1}$$

Then:

$$\ln \frac{c_0}{c} = \lambda t$$

$$\ln \left( \frac{1.000}{c} \right) = 2.875 \times 10^{-5} \text{ y}^{-1} \times 4.7 \times 10^9 \text{ y}$$

$$\ln c = -1.351 \times 10^5$$

$$c = 0$$

This calculation shows that no Pu-239 could remain since the formation of the earth. Consequently, the plutonium now present could not have been formed with the uranium.

25. Find the mass difference of the starting mass and the total masses of the final products. Then use the conversion for mass to energy to find the energy released:



$$8.0246 - 8.0053 - 0.00055 = 0.01875 \text{ amu}$$

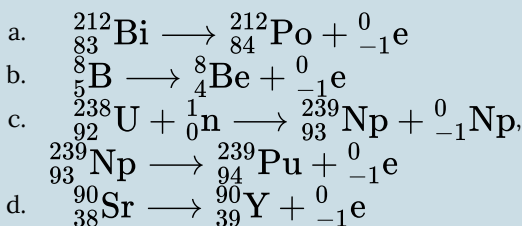
$$0.01875 \text{ amu} \times 1.6605 \times 10^{-27} \text{ kg/amu} = 3.113 \times 10^{-29} \text{ kg}$$

$$E = mc^2 = (3.113 \times 10^{-29} \text{ kg})(2.9979 \times 10^8 \text{ m/s})^2$$

$$= 2.798 \times 10^{-12} \text{ kg m}^2/\text{s}^2 = 2.798 \times 10^{-12} \text{ J/nucleus}$$

$$2.798 \times 10^{-12} \text{ J/nucleus} \times \frac{1 \text{ MeV}}{1.602177 \times 10^{-13} \text{ J}} = 17.5 \text{ MeV}$$

27. The balanced equations are as follows:



## Glossary

**alpha ( $\alpha$ ) decay:** loss of an alpha particle during radioactive decay

**beta ( $\beta$ ) decay:** breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

**daughter nuclide:** nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

**electron capture:** combination of a core electron with a proton to yield a neutron within the nucleus

**gamma ( $\gamma$ ) emission:** decay of an excited-state nuclide accompanied by emission of a gamma ray

**half-life ( $t_{1/2}$ ):** time required for half of the atoms in a radioactive sample to decay

**parent nuclide:** unstable nuclide that changes spontaneously into another (daughter) nuclide

**positron emission:** (also,  $\beta^+$  decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

**radioactive decay:** spontaneous decay of an unstable nuclide into another nuclide

**radioactive decay series:** chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

**radiocarbon dating:** highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  in the object vs. the ratio of  ${}^{14}_6\text{C} : {}^{12}_6\text{C}$  in the present-day atmosphere

**radiometric dating:** use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

PART XII

# THERMOCHEMISTRY



## 47. 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 1). 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.



Figure 1. 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 “Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner)

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 such as 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.

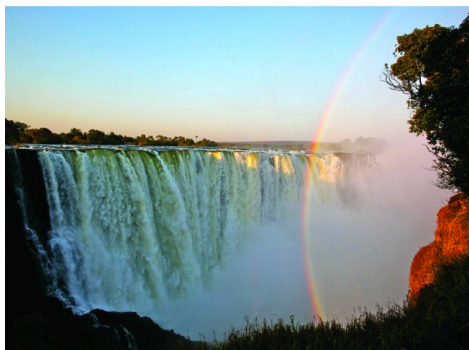
This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. 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 endeavor 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.

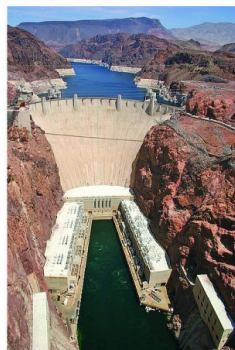
## Energy

**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 2). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a)



(b)

Figure 2. (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a 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 shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons)

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 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 3). 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.

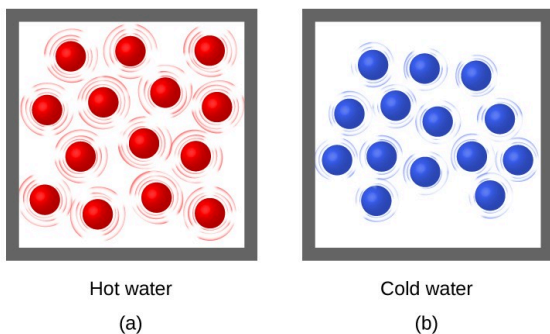


Figure 3. (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Click on this [PhET interactive simulation to view the effects of temperature on molecular motion](#).

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. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

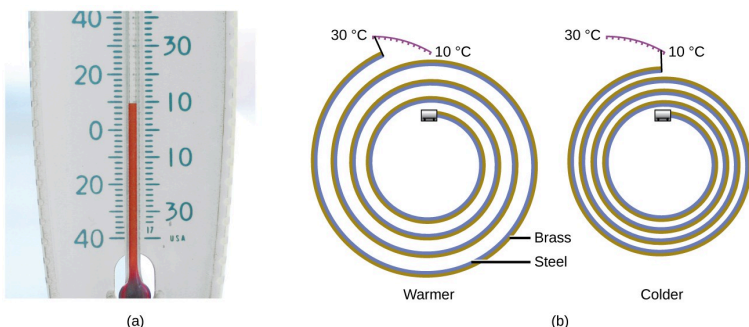


Figure 4. (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. 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”/Flickr)

This [link to a demonstration on Wikipedia](#) allows one to view the effects of heating and cooling a coiled bimetallic strip.

**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 5).

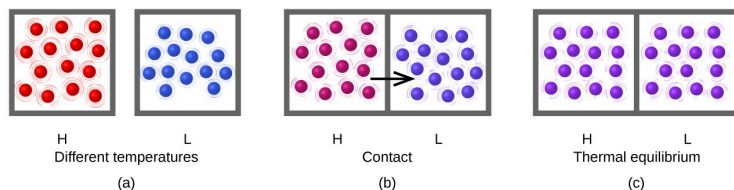


Figure 5. (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach “thermal equilibrium” when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Click on the [PhET simulation to explore energy forms and changes](#). Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

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 6). 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.



Figure 6. (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 the 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”/Wikimedia commons)

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 (1 kelvin). 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 named in honor of the English physicist James Prescott Joule. One joule is equivalent to  $1 \text{ kg m}^2/\text{s}^2$ , 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 ( $\Delta T$ ) 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



*Figure 7. 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)*

derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 7).

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 1.

**Table 1. 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 <sub>2</sub> O(l)	4.184
ethanol	C <sub>2</sub> H <sub>6</sub> O(l)	2.376
ice	H <sub>2</sub> O(s)	2.093 (at -10 °C)
water vapor	H <sub>2</sub> O(g)	1.864
nitrogen	N <sub>2</sub> (g)	1.040
air		1.007
oxygen	O <sub>2</sub> (g)	0.918
aluminum	Al(s)	0.897
carbon dioxide	CO <sub>2</sub> (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:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$

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

In this equation,  $c$  is the specific heat of the substance,  $m$  is its mass, and  $\Delta T$  (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 1: Measuring Heat*

A flask containing  $8.0 \times 10^2$  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?

Show Answer

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 20 °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 65 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation

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

:

$$\begin{aligned}
 &= (4.184\text{J/g}^\circ\text{C}) \times (800\text{g}) \times (85 - 20)^\circ\text{C} \\
 &= (4.184\text{J/g}^\circ\text{C}) \times (800\text{g}) \times (65)^\circ\text{C} \\
 &= 220,000\text{ J} (= 210\text{ kJ})
 \end{aligned}$$

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

### *Check Your Learning*

How much heat, in joules, must be added to a  $5.00 \times 10^2$ -g iron skillet to increase its temperature from  $25^\circ\text{C}$  to  $250^\circ\text{C}$ ? The specific heat of iron is  $0.451\text{ J/g}^\circ\text{C}$

Show Answer

$$5.05 \times 10^4\text{ J}$$

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.

### *Example 2: 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  $22.4^\circ\text{C}$  to  $43.6^\circ\text{C}$ . Determine the specific heat of this metal (which might provide a clue to its identity).

Show Answer

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 5.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

### *Check Your Learning*

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.

Show Answer

$c = 0.45 \text{ J/g }^{\circ}\text{C}$ ; the metal is likely to be iron

## Exercises

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) =  $3.6 \times 10^6$  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)?

Show Answer

We assume that the density of water is 1.0 g/cm<sup>3</sup> (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. First, find the mass of water in the bed. The volume is 72 in. × 84 in. × 9 in.

$$= 54,432 \text{ in.}^3 \left( \frac{2.54 \text{ cm}}{1 \text{ in.}} \right)^3 = 8.9 \times 10^5 \text{ cm}^3 \rightarrow 8.9 \times 10^5 \text{ g}$$

second, convert the change of 13 °F to °C:

$$q = cm\Delta T = 4.184 \text{ J/g}^\circ\text{C}(8.92 \times 10^5 \text{ g}) \times 7.22^\circ\text{C}$$
$$^\circ\text{C} = \frac{5^\circ}{9} \text{ F} = \frac{5}{9} \times 13 = 7.22^\circ\text{C} = 2.69 \times 10^7 \text{ J}$$

$$\text{Energy required} = \frac{2.689 \times 10^7 \text{ J}}{3.6 \times 10^6 \text{ kWh}^{-1}} = 7.47 \text{ kWh}$$

## 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 8). 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.

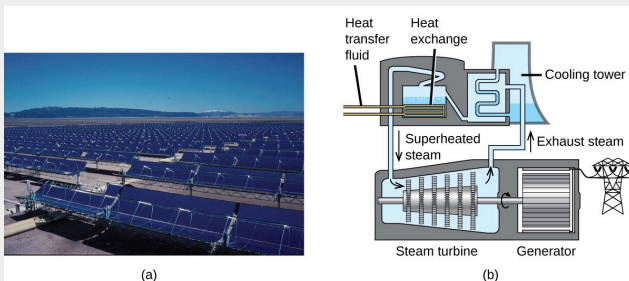


Figure 8. This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

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 9). 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.



(a)



(b)

Figure 9. (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; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

## Key Concepts and Summary

Energy is the capacity to 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).

Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between

objects at different temperatures; it flows from a high to a low temperature. 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.

### *Key Equations*

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

### *Exercises*

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?
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.
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
6. How much heat, in joules and in calories, must be added to a 75.0-g iron block with a specific heat of  $0.449 \text{ J/g } ^\circ\text{C}$  to increase its temperature from  $25 \text{ }^\circ\text{C}$  to its melting temperature of  $1535 \text{ }^\circ\text{C}$ ?
7. How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from  $-23.0 \text{ }^\circ\text{C}$  to  $-1.0 \text{ }^\circ\text{C}$ ?
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?
10. A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from  $23.2 \text{ }^\circ\text{C}$  to  $89.6 \text{ }^\circ\text{C}$ .
- a. What is the specific heat of the substance?
  - b. If it is one of the substances found in Table 1, what is its likely identity?
11. A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from  $19.3 \text{ }^\circ\text{C}$  to  $68.9 \text{ }^\circ\text{C}$ .
- a. What is the specific heat of the substance?
  - b. If it is one of the substances found in Table 1,

what is its likely identity?

12. An aluminum kettle weighs 1.05 kg.
- What is the heat capacity of the kettle?
  - How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °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 a specific heat of 4.184 J/g °C)?

#### Show Selected Answers

1. 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.

3. 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.

5. The heat capacity for each is as follows:

- $45.8 \cancel{\text{g}} \times 1.04 \text{J} / \cancel{\text{g}} \text{ } ^\circ\text{C} = 47.6 \text{J} / ^\circ\text{C}; 47.6 \cancel{\text{g}} \times 1.04 \text{J} \cancel{\text{g}}^{-1} \text{ } ^\circ\text{C}^{-1} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 11.38 \text{ J} ^\circ\text{C}^{-1}$
- $454 \text{ g} \times 0.897 \text{J} / \text{g} ^\circ\text{C} = 407 \text{ J} / ^\circ\text{C}; 454 \cancel{\text{g}} \times 0.897 \text{J} \cancel{\text{g}}^{-1} \text{ } ^\circ\text{C}^{-1} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 97.3 \text{ cal } ^\circ\text{C}^{-1}$

7.  $q = cm\Delta T$ ;  $q = 2.093 \text{ J/g } ^\circ\text{C} \times 28.4 \text{ g} \times [-1 - (-23)] ^\circ\text{C} = 1308 \text{ J}$  (or 1310 with the correct number of significant digits); the conversion factor is  $4.184 \text{ J} = 1 \text{ cal}$ ;  $1308 \text{ J} \times 1 \text{ cal} / 4.184 \text{ J} = 881.2 \text{ J}$  (881 J with the correct number of significant digits)

9.  $q = cm\Delta T$

$14,500 \text{ J} = 4.184 \text{ J g}^{-1} ^\circ\text{C} \times 4.85 \times 10^2 \text{ g} \times \Delta T$

$$\Delta T = \frac{14,500 ^\circ\text{C}}{4.184 \times 4.85 \times 10^2} = 7.15 ^\circ\text{C}$$

11. The answers are as follows:

- a.  $q = cm\Delta T$ ,  $c = q/(m\Delta T) = 8460 \text{ J} / [437.2 \text{ g} (68.9 - 19.3) ^\circ\text{C}] = 0.390 \text{ J/g } ^\circ\text{C}$
- b. Copper is a likely candidate.

## Glossary

**calorie (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

**endothermic process:** chemical reaction or physical change that absorbs heat

**energy:** capacity to supply heat or do work

**exothermic process:** chemical reaction or physical change that releases heat

**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)

**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,  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}$  and  $4.184 \text{ J} = 1 \text{ cal}$

**kinetic energy:** energy of a moving body, in joules, equal to  $\frac{1}{2}mv^2$  (where  $m$  = mass and  $v$  = velocity)

**potential energy:** energy of a particle or system of particles derived from relative position, composition, or condition

**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)

**temperature:** intensive property of matter that is a quantitative measure of “hotness” and “coldness;” it is related to the average kinetic energy of the atoms or molecules that make up the object

**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

**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

## 48. 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.

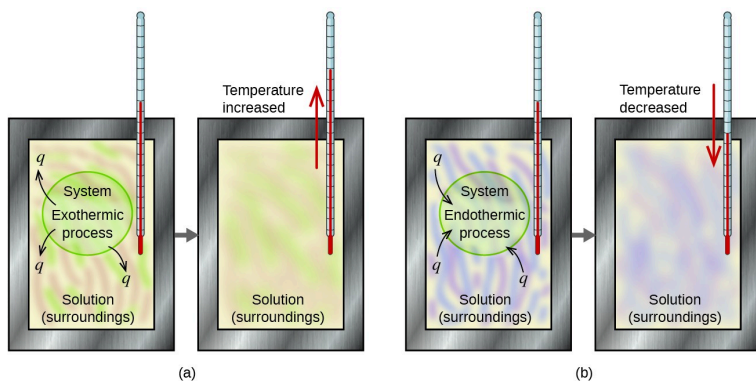
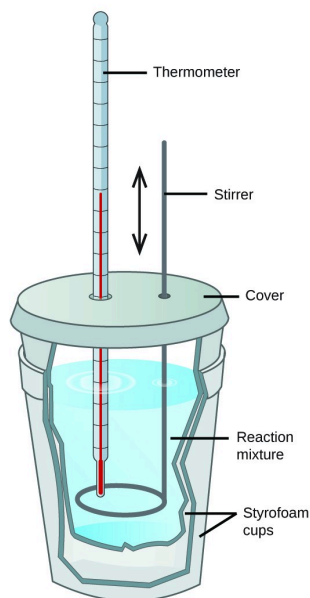


Figure 1. In a calorimetric determination, either (a) an exothermic process occurs and heat,  $q$ , is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat,  $q$ , is positive, indicating that thermal energy is transferred from the surroundings to the system.

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 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 1). 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.

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 2). These easy-to-use “coffee cup” calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.

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



*Figure 2. A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.*

vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure 3).

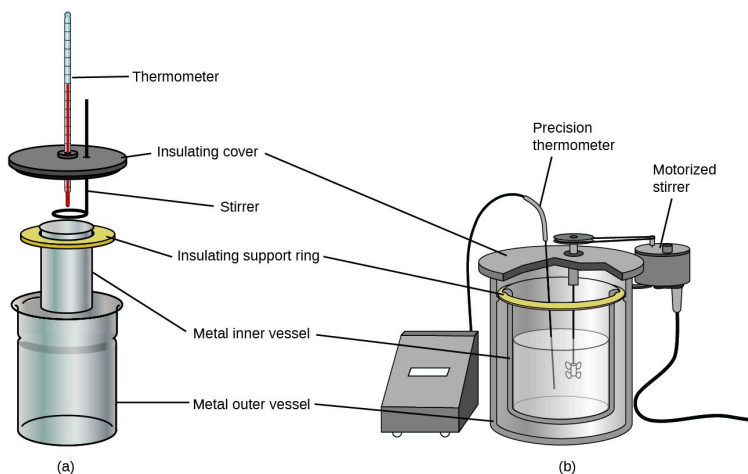


Figure 3. Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

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). 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.

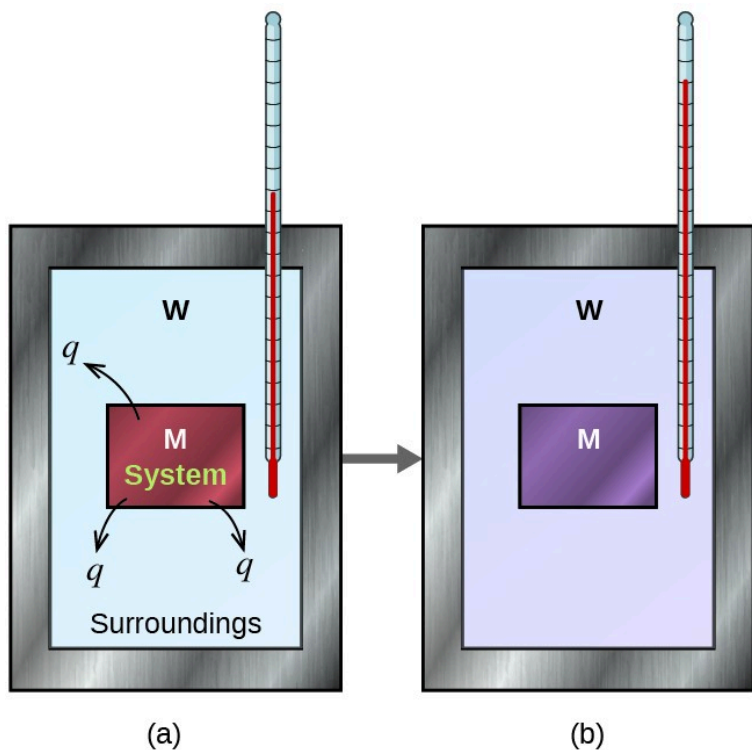


Figure 4. In a simple calorimetry process, (a) heat,  $q$ , is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

### Example 1: 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, and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Show Answer

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  $T_{\text{i, rebar}} = 248^\circ\text{C}$ , so the initial temperature of the rebar was  $248^\circ\text{C}$ .

### *Check Your Learning*

A 248-g piece of copper is dropped into 390 mL of water at  $22.6^\circ\text{C}$ . The final temperature of the water was measured as  $39.9^\circ\text{C}$ . Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Show Answer

The initial temperature of the copper was  $317^\circ\text{C}$ .

### *Check Your Learning*

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

Show Answer

The final temperature (reached by both copper and water) is  $38.8^\circ\text{C}$ .

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

## Example 2: 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.

Show Answer

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:

$$(c_{\text{metal}}) (59.7\text{g}) (28.5^\circ\text{C} - 100.0^\circ\text{C}) = - (4.18\text{J/g}^\circ\text{C}) (60.0\text{g}) (28.5^\circ\text{C} - 22.0^\circ\text{C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.18\text{J/g}^\circ\text{C}) (60.0\text{g}) (6.5^\circ\text{C})}{(59.7\text{g}) (-71.5^\circ\text{C})} = 0.38\text{J/g}^\circ\text{C}$$

Comparing this with values in Table 5.1, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

## Check Your Learning

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).

Show Answer

$$c_{\text{metal}} = 0.13 \text{ J/g } ^\circ\text{C}$$

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.

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”),  $q_{\text{reaction}}$ , plus the heat absorbed or lost by the solution (the “surroundings”),  $q_{\text{solution}}$ , must add up to zero:

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

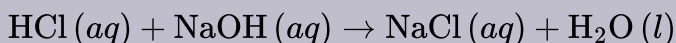
This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

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

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

### Example 3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M  $\text{HCl}(aq)$  and 50.0 mL of 0.10 M  $\text{NaOH}(aq)$ , 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



Show Answer

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  $\text{HCl}$  and  $\text{NaOH}$  at 22.0 °C. The  $\text{HCl}$  and  $\text{NaOH}$  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  $1.0 \times 10^2$  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.

### *Check Your Learning*

When 100 mL of 0.200 M NaCl(aq) and 100 mL of 0.200 M AgNO<sub>3</sub>(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?

Show Answer

1.31 × 10<sup>3</sup> 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

## Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 5). A common reusable hand warmer contains a supersaturated solution of  $\text{NaC}_2\text{H}_3\text{O}_2$  (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable  $\text{NaC}_2\text{H}_3\text{O}_2$  quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process  
 $\text{NaC}_2\text{H}_3\text{O}_2 (aq) \rightarrow \text{NaC}_2\text{H}_3\text{O}_2 (s)$  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  $\text{NaC}_2\text{H}_3\text{O}_2$  redissolves and can be reused.

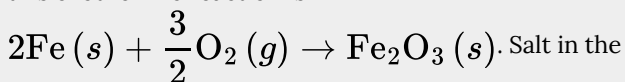


Figure 5. Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

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



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.

This [Wikimedia video shows the precipitation reaction](#) that occurs when the disk in a chemical hand warmer is flexed.

### *Example 4: 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 6). When 3.21 g of solid  $\text{NH}_4\text{NO}_3$  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 6. An instant cold pack consists of a bag containing solid ammonium nitrate and a 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.

Show Answer

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:

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

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

### *Check Your Learning*

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

Show Answer

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

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 7).

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

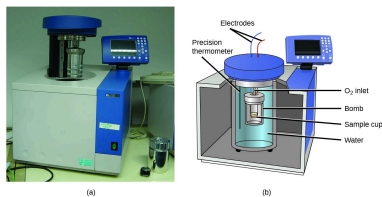


Figure 7. (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight “bomb,” which is submerged in water and surrounded by insulating materials. (credit a: modification of work by “Harbor1”/Wikimedia commons)

generally performed each time before the calorimeter is used to gather research data.

Watch this video on how a bomb calorimeter is prepared for action.



One or more interactive elements has been excluded from this version of the text. You can view them online here:

<https://library.achievingthedream.org/sanjacintroductorychemistry/?p=75#oembed-1>

[The Oxygen Bomb Calorimeter website](#) shows calorimetric calculations using sample data.

### *Example 5: Bomb Calorimetry*

When 3.12 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , 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?

Show Answer

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:

$$\begin{aligned}q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\&= -[(4.184\text{J/g}^\circ\text{C}) \times (775\text{g}) \times (35.6^\circ\text{C} - 23.8^\circ\text{C}) + 893\text{J/g}^\circ\text{C} \times (35.6^\circ\text{C} - 23.8^\circ\text{C})] \\&= -(38,200\text{J} + 10,500\text{J}) \\&= -48,700\text{J} = -48.7\text{kJ}\end{aligned}$$

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

### *Check Your Learning*

When 0.963 g of benzene,  $\text{C}_6\text{H}_6$ , is burned in a bomb calorimeter, the temperature of the calorimeter increases by  $8.39^\circ\text{C}$ . The bomb has a heat capacity of  $784\text{ J}/^\circ\text{C}$  and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Show Answer

39.0 kJ

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person. 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, different

dietary regimes, and with 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.

## 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.)

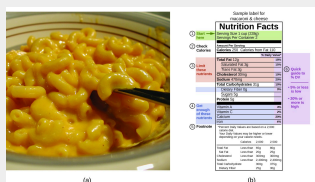


Figure 8. (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

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 8).

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 bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Click on [this link to access the US Department of Agriculture \(USDA\) National Nutrient Database](#), containing nutritional information on over 8000 foods.

## *Key Concepts and Summary*

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.

## *Exercises*

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.

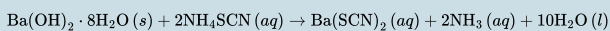
2. Would the amount of heat measured for the reaction in Example 5 be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.
3. Would the amount of heat absorbed by the dissolution in Example 6 appear greater, lesser, 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 6 appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

5. How many milliliters of water at  $23\text{ }^{\circ}\text{C}$  with a density of  $1.00\text{ g/mL}$  must be mixed with  $180\text{ mL}$  (about 6 oz) of coffee at  $95\text{ }^{\circ}\text{C}$  so that the resulting combination will have a temperature of  $60\text{ }^{\circ}\text{C}$ ? Assume that coffee and water have the same density and the same specific heat.
6. How much will the temperature of a cup ( $180\text{ g}$ ) of coffee at  $95\text{ }^{\circ}\text{C}$  be reduced when a  $45\text{ g}$  silver spoon (specific heat  $0.24\text{ J/g }^{\circ}\text{C}$ ) at  $25\text{ }^{\circ}\text{C}$  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  $45\text{-g}$  aluminum spoon (specific heat  $0.88\text{ J/g }^{\circ}\text{C}$ ) at  $24\text{ }^{\circ}\text{C}$  is placed in  $180\text{ mL}$  ( $180\text{ g}$ ) of coffee at  $85\text{ }^{\circ}\text{C}$  and the temperature of the two become 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  $88\text{ }^{\circ}\text{C}$ . 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  $240\text{ }^{\circ}\text{F}$ . After it passes through the radiator it has a temperature of  $175\text{ }^{\circ}\text{F}$ . Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of  $4.184\text{ J/g }^{\circ}\text{C}$ .
9. A  $70.0\text{-g}$  piece of metal at  $80.0\text{ }^{\circ}\text{C}$  is placed in  $100\text{ g}$  of water at  $22.0\text{ }^{\circ}\text{C}$  contained in a calorimeter like that shown in Figure 5.12. The metal and water come to the same temperature at  $24.6\text{ }^{\circ}\text{C}$ . 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 5.12, what is the resulting temperature of the water?
11. A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter (Figure 5.12). 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  $\text{CaCl}_2(\text{s})$  in 150.0 g of water in a calorimeter (Figure 5.12) 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?
13. When 50.0 g of 0.200 M  $\text{NaCl}(\text{aq})$  at 24.1 °C is added to 100.0 g of 0.100 M  $\text{AgNO}_3(\text{aq})$  at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as  $\text{AgCl}(\text{s})$  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  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  to a solution of 1.52 g of  $\text{NH}_4\text{SCN}$  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:



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  $\text{NH}_4\text{NO}_3$  in Example 4 were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.
17. When 1.0 g of fructose,  $\text{C}_6\text{H}_{12}\text{O}_6(s)$ , 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),  $\text{C}_7\text{H}_5\text{N}_2\text{O}_6$ , 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?
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 5.17), the

temperature increases by  $1.48\text{ }^{\circ}\text{C}$ . If the heat capacity of the calorimeter is  $21.6\text{ kJ}/^{\circ}\text{C}$ , determine the heat produced by combustion of a ton of coal  $2.000 \times 10^3$  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?
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  $1.1 \times 10^3$  Calories if the average number of Calories for fat is 9.1 Calories/g?
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,  $0.6919\text{ g/mL}$ ) that costs \$0.45?

Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

Show Selected Answers

2. lesser; more heat would be lost to the coffee cup and the environment and so  $\Delta T$  for the water would be lesser and the calculated  $q$  would be lesser

4. 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."  $q_{\text{rxn}} = -(q_{\text{solution}} + q_{\text{calorimeter}})$ ; since both  $q_{\text{solution}}$  and  $q_{\text{calorimeter}}$  are negative, including the latter term ( $q_{\text{rxn}}$ ) will yield a greater value for the heat of the dissolution

6. Because of the law of conservation of energy, we write:

$$q_{\text{spoon}} + q_{\text{coffee}} = 0; q_{\text{spoon}} = -q_{\text{coffee}} c_{\text{spoon}} \times m_{\text{spoon}} \times \Delta T = -c_{\text{coffee}} \times m_{\text{coffee}} \times \Delta T$$

$$0.24 \text{ J/g}^\circ\text{C} \times 45 \text{ g} \times (T_f - 25^\circ\text{C}) = 4.184 \text{ J/g}^\circ\text{C} \times 180 \text{ g} \times (T_f - 95^\circ\text{C})$$

$$10.8T_f - 270 = -753.1T_f + 71546.4$$

$$763.9 T_f = 71816.4$$

$$T_f = 94^\circ\text{C}.$$

The temperature of the coffee will drop 1 degree.

8. First, find the change in temperature of the water in  $^\circ\text{C}$ :

$$240^\circ\text{F} - 175^\circ\text{F} = 65^\circ\text{F}.$$

We are concerned here only with the difference between



temperatures and not the conversion from one temperature to the corresponding temperature.

$$^{\circ}\text{C} = \frac{5}{9}(^{\circ}\text{F}) = \frac{5}{9}(65) = 36.1^{\circ}\text{C}$$

Assuming 1 mL of water has a mass of 1 g, 1.0 gal of water has a mass of:

$$1.0 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{0.9463 \text{ L}}{1 \text{ qt}} \times 1000 \text{ g} = 3785 \text{ g}$$

$$q = cm\Delta T = 4.184 \text{ J/g}^{\circ}\text{C} \times 3785 \text{ g} \times 36.1^{\circ}\text{C} \\ = 5.7 \times 10^2 \text{ kJ.}$$

$$10. q = cm\Delta T = 4.184 \text{ J/g}^{\circ}\text{C} \times 30.0 \text{ g} \times (T_f - 26.5^{\circ}\text{C}) = 1506 \text{ J} \\ T_f - 26.5^{\circ}\text{C} = 1506 \text{ J} / (4.184 \text{ J/g}^{\circ}\text{C} \times 30.0 \text{ g}) = 12.0^{\circ}\text{C} \\ T_f = 26.5^{\circ}\text{C} + 12.0^{\circ}\text{C} = 38.5^{\circ}\text{C}$$

12. Assume that the mass of the added  $\text{CaCl}_2$  in solution must be added to the mass of the water:

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

$$q_{\text{reaction}} = -q_{\text{solution}} \quad q_{\text{solution}} = cm\Delta T$$

$$= 4.18 \text{ J/g}^{\circ}\text{C} \times 153.0 \text{ g} \times (25.8 - 22.4)^{\circ}\text{C} = 2200 \text{ J} \\ = 2.2 \text{ kJ.}$$

The heat produced shows that the reaction is exothermic.

$$14. q = cm\Delta T \\ = 4.20 \text{ J/g}^{\circ}\text{C} \times (3.15 + 1.52 + 100) \text{ g} \times 3.1^{\circ}\text{C} \\ = 1362.8 \text{ J} = 1.4 \text{ kJ (two significant figures)}$$

16. The heat of the reaction would be approximately the same as before or  $1.0 \times 10^3 \text{ J}$ . The reaction is endothermic, and the temperature would decrease:

$$q_{\text{rxn}} = -q_{\text{soln}} = -(c \times m \times \Delta T)_{\text{soln}} \\ -(4.18 \text{ J/g}^{\circ}\text{C}) \times (103.2 \text{ g}) \times (T_f - 24.9^{\circ}\text{C}) = 1000 \text{ J}$$

$$T_f - 24.9\text{ }^{\circ}\text{C} = -2.3\text{ }^{\circ}\text{C}$$

$$T_f = 22.6.$$

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.

18. The heat absorbed by the calorimeter is  $q_1 = 534\text{ J}/^{\circ}\text{C} \times (26.9\text{ }^{\circ}\text{C} - 23.4\text{ }^{\circ}\text{C}) = 1869\text{ J}$ . The heat absorbed by water is  $q_1 = 675\text{ mL} \times 0.997\text{ g/mL} \times 4.184\text{ J/g }^{\circ}\text{C} \times (26.9\text{ }^{\circ}\text{C} - 23.4\text{ }^{\circ}\text{C}) = 9855\text{ J}$ . The overall amount of heat  $q = q_1 + q_1 = 11,724\text{ J}$  or  $11.7\text{ kJ}$  with three significant digits.

20. Energy released by burning fat is:  
 $65\text{ g} \times 9.1\text{ Calories/g} = 5.9 \times 10^2\text{ Calories}$   
 $\% \text{ Calories from fat} = 5.9 \times 10^2\text{ Calories} / 2000\text{ Calories} \times 100\%$   
 $= 30\%$  (one significant figure).

22. The average energy from carbohydrates is  $4.1\text{ kcal/g}$  ( $4.1\text{ Calories/g}$ ). The drink cannot contain more than

$$\frac{1\text{ Calorie}}{4.1\text{ Calorie g}^{-1}} = 0.24\text{g}$$

24.	
Protein: $3\text{g} \times 4.1\text{Calories/g}$	12.3Calories
Carbohydrates: $18\text{g} \times 4.1\text{Calories/g}$	73.8Calories
Fat: $6\text{g} \times 9.1\text{Calories/g}$	<u>54.6Calories</u>
	140.7Calories
Total = $1.4 \times 10^2\text{Calories}$	

## Glossary

**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

**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

**nutritional calorie (Calorie):** unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

**surroundings:** all matter other than the system being studied

**system:** portion of matter undergoing a chemical or physical change being studied



PART XIII

ACIDS, BASES AND PH



# 49. Acids and Bases

## *Learning Objectives*

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

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

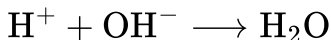
Acids and bases have been known for a long time. When Robert **Boyle** characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact 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  $\text{CO}_2$ ), 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. 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) and a base as a compound that dissolves in water to yield hydroxide anions.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions ( $\text{H}_3\text{O}^+$ ) and a base as a compound that dissolves in water to yield hydroxide ions ( $\text{OH}^-$ ). This definition is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton,  $\text{H}^+$ . A proton is what remains when a normal hydrogen atom,  ${}_1^1\text{H}$ , 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). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

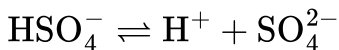
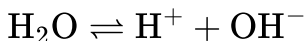
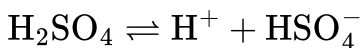
Acids may be compounds such as  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , organic acids like acetic acid ( $\text{CH}_3\text{COOH}$ ) or ascorbic acid (vitamin C), or  $\text{H}_2\text{O}$ . Anions (such as  $\text{HSO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HS}^-$ , and  $\text{HCO}_3^-$ ) and cations (such as  $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$ , and  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_3\text{NH}_2$ ), anions (such as  $\text{OH}^-$ ,  $\text{HS}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{F}^-$ , and  $\text{PO}_4^{3-}$ ), or cations (such as  $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ ). The most familiar bases are ionic compounds such as  $\text{NaOH}$  and  $\text{Ca}(\text{OH})_2$ , which contain the hydroxide ion,  $\text{OH}^-$ . The hydroxide ion in these compounds accepts a proton from acids to form water:



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):

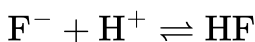
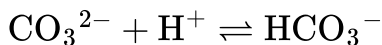
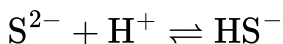
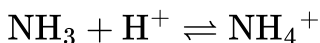
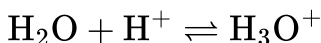
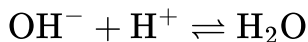


acid  $\rightleftharpoons$  proton + conjugate base

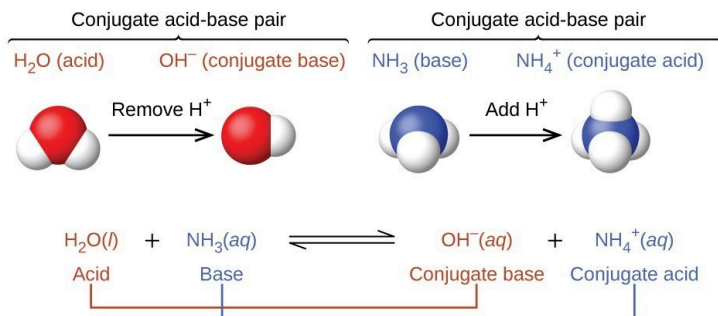


We call the product that results when a base accepts a proton the base's conjugate acid. This species is an acid because it can give up a proton (and thus re-form the base):

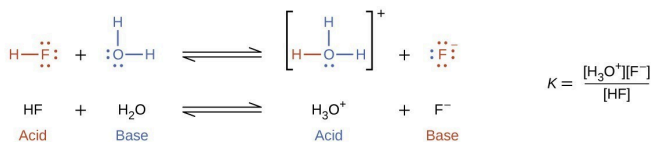
base + proton  $\rightleftharpoons$  conjugate acid



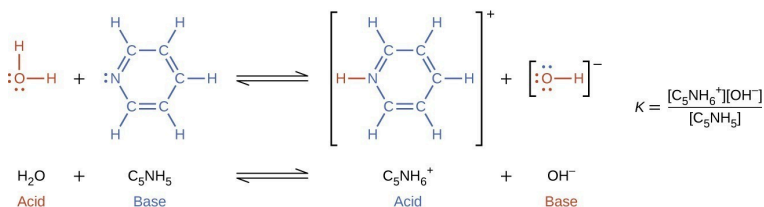
In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the *transfer* of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water,  $\text{OH}^-$ , and the conjugate acid of ammonia,  $\text{NH}_4^+$  :



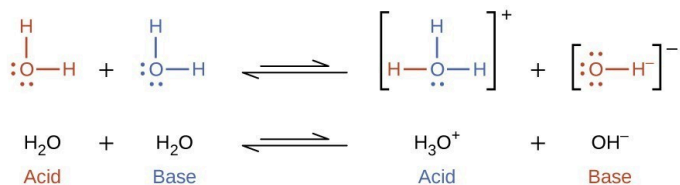
The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



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 ammonia to water yields hydroxide ions and ammonium ions:

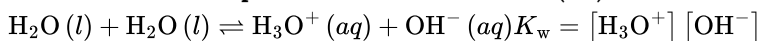


Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an 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:



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**.

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 equilibrium constant for the ionization of water is called the **ion-product constant for water ( $K_w$ )**:



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  $1.0 \times 10^{-14}$ . 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  $5.1 \times 10^{-13}$ , roughly 100-times larger than the value at 25 °C.

### Example 1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Show Answer

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water,

$[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . At 25 °C:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^{2+} = [\text{OH}^-]^{2+} = 1.0 \times 10^{-14}$$

So:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal  $1.0 \times 10^{-7} M$ .

### Check Your Learning

The ion product of water at 80 °C is  $2.4 \times 10^{-13}$ . What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Show Answer

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 4.9 \times 10^{-7} M$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example

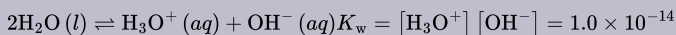
2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

### *Example 2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$*

A solution of carbon dioxide in water has a hydronium ion concentration of  $2.0 \times 10^{-6}M$ . What is the concentration of hydroxide ion at 25 °C?

Show Answer

We know the value of the ion-product constant for water at 25 °C:



Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the  $K_w$  expression yields that  $[OH^-]$  is directly proportional to the inverse of  $[H_3O^+]$ :

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to  $5.0 \times 10^{-9}M$  as the hydrogen ion concentration increases to  $2.0 \times 10^{-6}M$ . 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:

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = (2.0 \times 10^{-6}) (5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

### *Check Your Learning*

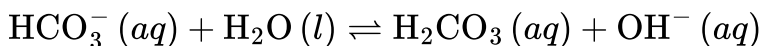
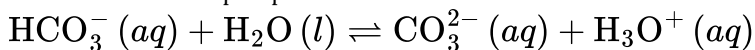
What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Show Answer

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-11} \text{ M}$$

## Amphiprotic Species

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:



### *Example 3: Representing the Acid-Base Behavior of an Amphoteric Substance*

Write separate equations representing the reaction of  $\text{HSO}_3^-$

1. as an acid with  $\text{OH}^-$
2. as a base with  $\text{HI}$

Show Answer

1.  $\text{HSO}_3^- (aq) + \text{OH}^- (aq) \rightleftharpoons \text{SO}_3^{2-} (aq) + \text{H}_2\text{O} (l)$
2.  $\text{HSO}_3^- (aq) + \text{HI} (aq) \rightleftharpoons \text{H}_2\text{SO}_3 (aq) + \text{I}^- (aq)$

### *Check Your Learning*

Write separate equations representing the reaction of  $\text{H}_2\text{PO}_4^-$

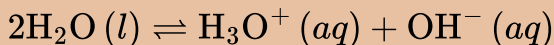
1. as a base with  $\text{HBr}$
2. as an acid with  $\text{OH}^-$

Show Answer

1.  $\text{H}_2\text{PO}_4^- (aq) + \text{HBr} (aq) \rightleftharpoons \text{H}_3\text{PO}_4 (aq) + \text{Br}^- (aq)$
2.  $\text{H}_2\text{PO}_4^- (aq) + \text{OH}^- (aq) \rightleftharpoons \text{HPO}_4^{2-} (aq) + \text{H}_2\text{O} (l)$

## *Key Concepts and Summary*

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,  $\text{H}_3\text{O}^+$ , and the hydroxide ion,  $\text{OH}^-$  when it undergoes autoionization:



The ion product of water,  $K_w$  is the equilibrium constant for the autoionization reaction:

$$K_w = [\text{H}_2\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

### *Key Equations*

- $$K_w = [\text{H}_2\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$



## Exercises

1. Write equations that show  $\text{NH}_3$  as both a conjugate acid and a conjugate base.
2. Write equations that show  $\text{H}_2\text{PO}_4^-$  acting both as an acid and as a base.
3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

- a.  $\text{H}_3\text{O}^+$
- b.  $\text{HCl}$
- c.  $\text{NH}_3$
- d.  $\text{CH}_3\text{CO}_2\text{H}$
- e.  $\text{NH}_4^+$
- f.  $\text{HSO}_4^-$

4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

- a.  $\text{HNO}_3$
- b.  $\text{PH}_4^+$
- c.  $\text{H}_2\text{S}$
- d.  $\text{CH}_3\text{CH}_2\text{COOH}$
- e.  $\text{H}_2\text{PO}_4^-$
- f.  $\text{HS}^-$

5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

- a.  $\text{H}_2\text{O}$

- b.  $\text{OH}^-$
  - c.  $\text{NH}_3$
  - d.  $\text{CN}^-$
  - e.  $\text{S}^{2-}$
  - f.  $\text{H}_2\text{PO}_4^-$
6. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
  - a.  $\text{HS}^-$
  - b.  $\text{PO}_4^{3-}$
  - c.  $\text{NH}_2^-$
  - d.  $\text{C}_2\text{H}_5\text{OH}$
  - e.  $\text{O}^{2-}$
  - f.  $\text{H}_2\text{PO}_4^-$
7. What is the conjugate acid of each of the following?  
What is the conjugate base of each?
  - a.  $\text{OH}^-$
  - b.  $\text{H}_2\text{O}$
  - c.  $\text{HCO}_3^-$
  - d.  $\text{NH}_3$
  - e.  $\text{HSO}_4^-$
  - f.  $\text{H}_2\text{O}_2$
  - g.  $\text{HS}^-$
  - h.  $\text{H}_5\text{N}_2^+$
8. What is the conjugate acid of each of the following?  
What is the conjugate base of each?
  - a.  $\text{H}_2\text{S}$
  - b.  $\text{H}_2\text{PO}_4^-$

- c.  $\text{PH}_3$
- d.  $\text{HS}^-$
- e.  $\text{HSO}_3^-$
- f.  $\text{H}_3\text{O}_2^+$
- g.  $\text{H}_4\text{N}_2$
- h.  $\text{CH}_3\text{OH}$

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.  $\text{HNO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$
- b.  $\text{CN}^- + \text{H}_2\text{O} \longrightarrow \text{HCN} + \text{OH}^-$
- c.  $\text{H}_2\text{SO}_4 + \text{Cl}^- \longrightarrow \text{HCl} + \text{HSO}_4^-$
- d.  $\text{HSO}_4^- + \text{OH}^- \longrightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$
- e.  $\text{O}^{2-} + \text{H}_2\text{O} \longrightarrow 2\text{OH}^-$
- f.  $[\text{Cu}(\text{H}_2\text{O})_3(\text{OH})]^+ + [\text{Al}(\text{H}_2\text{O})_6]^{3+} \longrightarrow [\text{Cu}(\text{H}_2\text{O})_4]^{2+} + [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$
- g.  $\text{H}_2\text{S} + \text{NH}_2^- \longrightarrow \text{HS}^- + \text{NH}_3$

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:

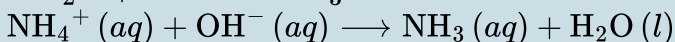
- a.  $\text{NO}_2^- + \text{H}_2\text{O} \longrightarrow \text{HNO}_2 + \text{OH}^-$
- b.  $\text{HBr} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Br}^-$
- c.  $\text{HS}^- + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{S} + \text{OH}^-$
- d.  $\text{H}_2\text{PO}_4^- + \text{OH}^- \longrightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$
- e.  $\text{H}_2\text{PO}_4^- + \text{HCl} \longrightarrow \text{H}_3\text{PO}_4 + \text{Cl}^-$
- f.  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + [\text{Al}(\text{H}_2\text{O})_6]^{3+} \longrightarrow [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$
- g.  $\text{CH}_3\text{OH} + \text{H}^- \longrightarrow \text{CH}_3\text{O}^- + \text{H}_2$

11. What are amphoteric species? Illustrate with suitable equations.

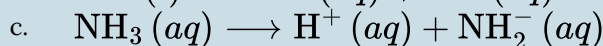
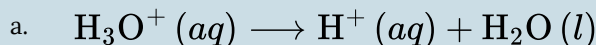
12. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:
- $\text{H}_2\text{O}$
  - $\text{H}_2\text{PO}_4^-$
  - $\text{S}^{2-}$
  - $\text{CO}_3^{2-}$
  - $\text{HSO}_4^-$
13. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.
- $\text{NH}_3$
  - $\text{HPO}_4^-$
  - $\text{Br}^-$
  - $\text{NH}_4^+$
  - $\text{ASO}_4^{3-}$
14. Is the self ionization of water endothermic or exothermic? The ionization constant for water ( $K_w$ ) is  $2.9 \times 10^{-14}$  at  $40^\circ\text{C}$  and  $9.6 \times 10^{-14}$  at  $60^\circ\text{C}$ .

Show Selected Answers

1. One example for  $\text{NH}_3$  as a conjugate acid:



3. The net ionic equations are as follows:



- d.  $\text{CH}_3\text{CO}_2\text{H} (aq) \longrightarrow \text{H}^+ (aq) + \text{CH}_3\text{CO}_2^- (aq)$
- e.  $\text{NH}_4^+ (aq) \longrightarrow \text{H}^+ (aq) + \text{NH}_3 (aq)$
- f.  $\text{HSO}_4^- (aq) \longrightarrow \text{H}^+ (aq) + \text{SO}_4^{2-} (aq)$

5. The net ionic equations are as follows:

- a.  $\text{H}_2\text{O} (l) + \text{H}^+ (aq) \longrightarrow \text{H}_3\text{O}^+ (aq)$
- b.  $\text{OH}^- (aq) + \text{H}^+ (aq) \longrightarrow \text{H}_2\text{O} (l)$
- c.  $\text{NH}_3 (aq) + \text{H}^+ (aq) \longrightarrow \text{NH}_4^+ (aq)$
- d.  $\text{CN}^- (aq) + \text{H}^+ (aq) \longrightarrow \text{HCN} (aq)$
- e.  $\text{S}^{2-} (aq) + \text{H}^+ (aq) \longrightarrow \text{HS}^- (aq)$
- f. (f)  
 $\text{H}_2\text{PO}_4^- (aq) + \text{H}^+ (aq) \longrightarrow \text{H}_3\text{PO}_4 (aq)$

7. The conjugate acids and bases are as follows:

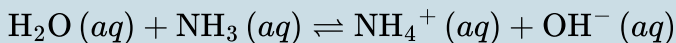
- a.  $\text{H}_2\text{O}, \text{O}^{2-}$
- b.  $\text{H}_3\text{O}^+, \text{OH}^-$
- c.  $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$
- d.  $\text{NH}_4^+, \text{NH}_2^-$
- e.  $\text{H}_2\text{SO}_4, \text{SO}_4^{2-}$
- f.  $\text{H}_3\text{O}_2^+, \text{HO}_2^-$
- g.  $\text{H}_2\text{S}, \text{S}^{2-}$
- h.  $\text{H}_6\text{N}_2^{2+}, \text{H}_4\text{N}_2$

9. The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA.

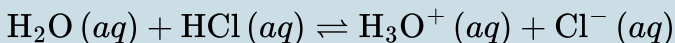
- a.  $\text{HNO}_3(\text{BA}), \text{H}_2\text{O}(\text{BB}), \text{H}_3\text{O}^+ (\text{CA}), \text{NO}_3^- (\text{CB})$
- b.  $\text{CN}^-(\text{BB}), \text{H}_2\text{O}(\text{BA}), \text{HCN}(\text{CA}), \text{OH}^-(\text{CB})$

- c.  $\text{H}_2\text{SO}_4(\text{BA}), \text{Cl}^-(\text{BB}), \text{HCl}(\text{CA}), \text{HSO}_4^-(\text{CB})$
- d.  $\text{HSO}_4^-(\text{BA}), \text{OH}^-(\text{BB}), \text{SO}_4^{2-}(\text{CB}), \text{H}_2\text{O}(\text{CA})$
- e.  $\text{O}^{2-}(\text{BB}), \text{H}_2\text{O}(\text{BA}), \text{OH}^-(\text{CB and CA})$
- f.  $[\text{Cu}(\text{H}_2\text{O})_3(\text{OH})]^+(\text{BB}),$   
 $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{BA}),$   
 $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}(\text{CA}),$   
 $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{CB})$
- g.  $\text{H}_2\text{S}(\text{BA}), \text{NH}_2^-(\text{BB}), \text{HS}^-(\text{CB}), \text{NH}_3(\text{CA})$

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  $\text{H}_2\text{O}$ . As an acid:



. As a base:



13. (a) and (b) are amphiprotic. (c), (d), and (e) are not amphiprotic.

- a.  $\text{NH}_3 + \text{H}_3\text{O}^+ \longrightarrow \text{NH}_4\text{OH} + \text{H}_2\text{O},$   
 $\text{NH}_3 + \text{OCH}_3^- \longrightarrow \text{NH}_2^- + \text{CH}_3\text{OH}$
- b.  $\text{HPO}_4^{2-} + \text{OH}^- \longrightarrow \text{PO}_4^{3-} + \text{H}_2\text{O},$   
 $\text{HPO}_4^{2-} + \text{HClO}_4 \longrightarrow \text{H}_2\text{PO}_4^- + \text{ClO}_4^-$
- c.  $\text{Br}^-$
- d.  $\text{NH}_4^+$
- e.  $\text{AsO}_4^{3-}$

## Glossary

**acid ionization:** reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

**amphiprotic:** species that may either gain or lose a proton in a reaction

**amphoteric:** species that can act as either an acid or a base

**autoionization:** reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

**base ionization:** reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

**Brønsted-Lowry acid:** proton donor

**Brønsted-Lowry base:** proton acceptor

**conjugate acid:** substance formed when a base gains a proton

**conjugate base:** substance formed when an acid loses a proton

**ion-product constant for water ( $K_w$ ):** equilibrium constant for the autoionization of water

## 50. pH and pOH

### *Learning Objectives*

By the end of this module, 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 behaviors 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.

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:



$$pX = -\log X$$

The pH of a solution is therefore defined as shown here, where  $[H_3O^+]$  is the molar concentration of hydronium ion in the solution:

$$pH = -\log[H_3O^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[H_3O^+] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH**:

$$pOH = -\log[OH^-]$$

or

$$[OH^-] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the  $K_w$  expression:

$$K_w = [H_3O^+][OH^-]$$

$$-\log K_w = -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + -\log[OH^-]$$

$$pK_w = pH + pOH$$

At 25 °C, the value of  $K_w$  is  $1.0 \times 10^{-14}$ , and so:

$$14.00 = pH + pOH$$

As we learned earlier, the hydronium ion molarity in pure water (or any neutral solution) is  $1.0 \times 10^{-7}M$  at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than  $1.0 \times 10^{-7}M$  and hydroxide ion molarities less than  $1.0 \times 10^{-7}M$  (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  $1.0 \times 10^{-7}M$  and hydroxide ion molarities greater than  $1.0 \times 10^{-7}M$  (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 is 80 °C is  $4.9 \times 10^{-7}\text{M}$ , 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  $\text{pH} = \text{pOH} = 6.31$ , 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 1).

Table 1. Summary of Relations for Acidic, Basic and Neutral Solutions		
Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	$\text{pH} < 7$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$\text{pH} = 7$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	$\text{pH} > 7$

Figure 1 shows the relationships between  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

$[\text{H}_3\text{O}^+]$ (M)	$[\text{OH}^-]$ (M)	pH	pOH	Sample Solution
$10^1$	$10^{-15}$	-1	15	
$10^0$ or 1	$10^{-14}$	0	14	← 1 M HCl acidic
$10^{-1}$	$10^{-13}$	1	13	
$10^{-2}$	$10^{-12}$	2	12	← gastric juice ← lime juice ← 1 M $\text{CH}_3\text{CO}_2\text{H}$ (vinegar)
$10^{-3}$	$10^{-11}$	3	11	← stomach acid
$10^{-4}$	$10^{-10}$	4	10	← wine ← orange juice
$10^{-5}$	$10^{-9}$	5	9	← coffee
$10^{-6}$	$10^{-8}$	6	8	← rain water
$10^{-7}$	$10^{-7}$	7	7	← pure water neutral
$10^{-8}$	$10^{-6}$	8	6	← blood ← ocean water ← baking soda
$10^{-9}$	$10^{-5}$	9	5	
$10^{-10}$	$10^{-4}$	10	4	
$10^{-11}$	$10^{-3}$	11	3	← Milk of Magnesia
$10^{-12}$	$10^{-2}$	12	2	← household ammonia, $\text{NH}_3$ ← bleach
$10^{-13}$	$10^{-1}$	13	1	
$10^{-14}$	$10^0$ or 1	14	0	← 1 M NaOH basic
$10^{-15}$	$10^1$	15	-1	

Figure 1. The pH and pOH scales represent concentrations of  $[\text{H}_3\text{O}^+]$  and  $\text{OH}^-$ , respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

### Example 1: Calculation of pH from $[\text{H}_3\text{O}^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of  $1.2 \times 10^{-3}$  M?

Show Answer

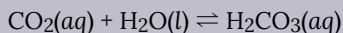
$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3})\end{aligned}$$

$$= -(-2.92) = 2.92$$

(The use of logarithms is explained in [Essential Mathematics](#). 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.)

### *Check Your Learning*

Water exposed to air contains carbonic acid,  $\text{H}_2\text{CO}_3$ , due to the reaction between carbon dioxide and water:



Air-saturated water has a hydronium ion concentration caused by the dissolved  $\text{CO}_2$  of  $2.0 \times 10^{-6}\text{M}$ , about 20-times larger than that of pure water. Calculate the pH of the solution at  $25^\circ\text{C}$ .

Show Answer

5.70

### *Example 2: Calculation of Hydronium Ion Concentration from pH*

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Show Solution

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.3$$

$$\log[\text{H}_3\text{O}^+] = -7.3$$

$$[\text{H}_3\text{O}^+] = 10^{-7.3} \text{ or } [\text{H}_3\text{O}^+] = \text{antilog of } -7.3$$

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-8} \text{ M}$$

(On a calculator take the antilog, or the “inverse” log, of  $-7.3$ , or calculate  $10^{-7.3}$ .)

### *Check Your Learning*

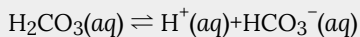
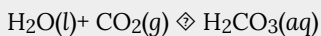
Calculate the hydronium ion concentration of a solution with a pH of  $-1.07$ .

Show Answer

12 M

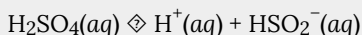
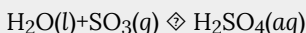
## Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved  $\text{CO}_2$  which forms carbonic acid:



Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including  $\text{CO}_2$ ,  $\text{SO}_2$ ,

SO<sub>3</sub>, NO, and NO<sub>2</sub> being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:



Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 2). Regulations limiting the amount of sulfur and nitrogen

oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this [US Environmental Protection Agency website](#).



(a)



(b)

Figure 2. (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

### Example 3: Calculation of $pOH$

What are the  $pOH$  and the  $pH$  of a 0.0125-M solution of potassium hydroxide,  $KOH$ ?

Show Answer

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding  $[\text{OH}^-] = 0.0125 \text{ M}$ :

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10$$

### *Check Your Learning*

The hydronium ion concentration of vinegar is approximately  $4 \times 10^{-3} \text{ M}$ . What are the corresponding values of pOH and pH?

Show Answer

$$\text{pOH} = 11.6, \text{pH} = 2.4$$

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 3).





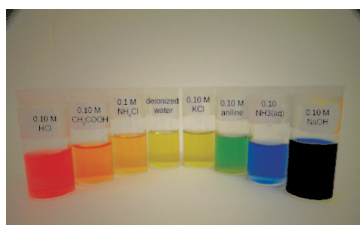
(a)



(b)

Figure 3. (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of  $\pm 0.002$  pH units, and may cost in excess of \$1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy ( $\pm 0.2$  pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 4).



(a)



(b)

Figure 4. (a) A universal indicator assumes a different color 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 = 1),  $\text{CH}_3\text{CO}_2\text{H}$  (pH = 3), and  $\text{NH}_4\text{Cl}$  (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline,  $\text{C}_6\text{H}_5\text{NH}_2$  (pH = 9),  $\text{NH}_3$  (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa)

## Key Concepts and Summary

The concentration of hydronium ion in a solution of an acid in water is greater than  $1.0 \times 10^{-7} \text{ M}$  at  $25^\circ \text{C}$ . The concentration of hydroxide ion in a solution of a base in water is greater than  $1.0 \times 10^{-7} \text{ M}$  at  $25^\circ \text{C}$ . The concentration of  $\text{H}_3\text{O}^+$  in a solution can be expressed as the pH of the solution;  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ . The concentration of  $\text{OH}^-$  can be expressed as the pOH of the solution:  $\text{pOH} = -\log[\text{OH}^-]$ . In pure water,  $\text{pH} = 7.00$  and  $\text{pOH} = 7.00$

## Key Equations

- $\text{pH} = -\log[\text{H}_3\text{O}^+]$
- $\text{pOH} = -\log[\text{OH}^-]$
- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
- $[\text{OH}^-] = 10^{-\text{pOH}}$
- $\text{pH} + \text{pOH} = \text{p}K_{\text{w}} = 14.00$  at  $25^\circ \text{C}$

## Exercises

1. Explain why a sample of pure water at  $40^\circ \text{C}$  is neutral even though  $[\text{H}_3\text{O}^+] = 1.7 \times 10^{-7} \text{ M}$ .  $K_{\text{w}}$  is  $2.9 \times 10^{-14}$  at  $40^\circ \text{C}$ .
2. The ionization constant for water ( $K_{\text{w}}$ ) is  $2.9 \times 10^{-14}$

- at 40 °C. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH for pure water at 40 °C.
3. The ionization constant for water ( $K_w$ ) is  $9.614 \times 10^{-14}$  at 60 °C. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH for pure water at 60 °C.
  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  $\text{HNO}_3$
    - d. 0.0031 M  $\text{Ca}(\text{OH})_2$
  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  $\text{HClO}_4$
    - b. 0.21 M NaOH
    - c. 0.000071 M  $\text{Ba}(\text{OH})_2$
    - d. 2.5 M KOH
  6. What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?
  7. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?
  8. Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 1 for useful information.
  9. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 1 for useful information.

10. The hydronium ion concentration in a sample of rainwater is found to be  $1.7 \times 10^{-6} \text{M}$  at  $25^\circ \text{C}$ . What is the concentration of hydroxide ions in the rainwater?
11. The hydroxide ion concentration in household ammonia is  $3.2 \times 10^{-3} \text{M}$  at  $25^\circ \text{C}$ . What is the concentration of hydronium ions in the solution?

Show Selected Answers

1. In a neutral solution  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . At  $40^\circ \text{C}$ ,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}.$$

$$3. \quad x = 3.101 \times 10^{-7} \text{M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

$$\text{pH} = -\log 3.101 \times 10^{-7} = -(-6.5085) = 6.5085$$

$$\text{pOH} = \text{pH} = 6.5085$$

5. The pH and the pOH are as follows:

$$\text{a.} \quad \text{pH} = 3.587; \text{pOH} = 10.413;$$

$$\text{b.} \quad \text{pH} = 0.68; \text{pOH} = 13.32;$$

$$\text{c.} \quad \text{pOH} = 3.85; \text{pH} = 10.15;$$

$$\text{d.} \quad \text{pH} = -0.40; \text{pOH} = 14.4$$

$$7. \quad [\text{H}_3\text{O}^+] = 3.0 \times 10^{-7} \text{M}; [\text{OH}^-] = 3.3 \times 10^{-8} \text{M}$$

$$9. \quad [\text{H}_3\text{O}^+] = 1 \times 10^{-2} \text{M}; [\text{OH}^-] = 1 \times 10^{-12} \text{M}$$

$$11. \quad [\text{OH}^-] = 3.1 \times 10^{-12} \text{M}$$

## Glossary

**acidic:** describes a solution in which  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

**basic:** describes a solution in which  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

**neutral:** describes a solution in which  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

**pH:** logarithmic measure of the concentration of hydronium ions in a solution

**pOH:** logarithmic measure of the concentration of hydroxide ions in a solution



PART XIV

# EQUILIBRIUM BASICS





# 51. Chemical Equilibria

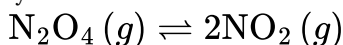
## *Learning Objectives*

By the end of this module, 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 ( $\text{N}_2\text{O}_4$ , a colorless gas) in a glass tube, it forms nitrogen dioxide ( $\text{NO}_2$ , a brown gas) by the reaction



The color becomes darker as  $\text{N}_2\text{O}_4$  is converted to  $\text{NO}_2$ . When the system reaches equilibrium, both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are present Figure 1.

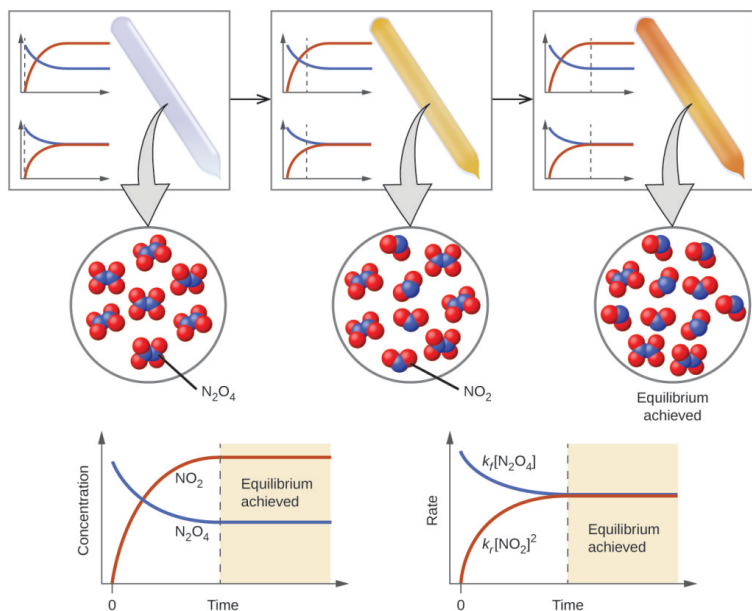


Figure 1. A mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  moves toward equilibrium. Colorless  $\text{N}_2\text{O}_4$  reacts to form brown  $\text{NO}_2$ . As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of  $\text{NO}_2$ .

The formation of  $\text{NO}_2$  from  $\text{N}_2\text{O}_4$  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  $\text{NO}_2$  from  $\text{N}_2\text{O}_4$ , are reversible under more



*Figure 2. 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.*

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  $\text{N}_2\text{O}_4$  decompose to form  $\text{NO}_2$ , but the  $\text{NO}_2$  produced can react to form  $\text{N}_2\text{O}_4$ . As soon as the forward reaction produces any  $\text{NO}_2$ , the reverse reaction begins and  $\text{NO}_2$  starts to react to form  $\text{N}_2\text{O}_4$ . At equilibrium, the concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  no longer change because the rate of formation of  $\text{NO}_2$  is exactly equal to the rate of consumption of  $\text{NO}_2$ , and the rate of formation of  $\text{N}_2\text{O}_4$  is exactly equal to the rate of consumption of  $\text{N}_2\text{O}_4$ .

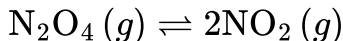
**Chemical equilibrium is a dynamic process:** As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them Figure 2.

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 1.

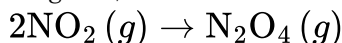
We can detect a state of equilibrium because the concentrations

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.

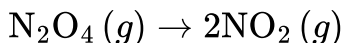
We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 1 shows the reaction:



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 1, the rate of the forward reaction



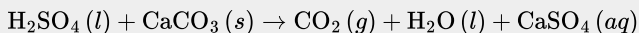
is equal to the rate of the backward reaction



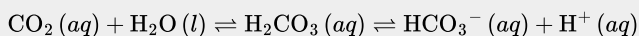
## Equilibrium and Soft Drinks

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  $\text{CO}_2$  falls into the container of water beneath the vessel in which

the initial reaction takes place; agitation helps the gaseous  $\text{CO}_2$  mix into the liquid water.



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 ( $\text{H}_2\text{CO}_3$ ). Since carbonic acid is a weak acid, it can dissociate into protons ( $\text{H}^+$ ) and hydrogen carbonate ions ( $\text{HCO}_3^-$ ).



Today,  $\text{CO}_2$  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  $\text{CO}_2$  gas in the air space on top of the bottle escapes, causing

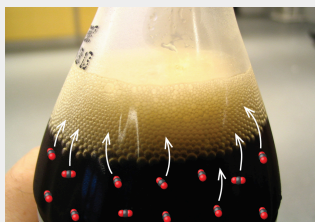
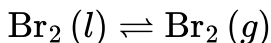


Figure 3. When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

the equilibrium between gas-phase  $\text{CO}_2$  and dissolved or aqueous  $\text{CO}_2$  to shift, lowering the concentration of  $\text{CO}_2$  in the soft drink. Less  $\text{CO}_2$  dissolved in the liquid leads to carbonic acid decomposing to dissolved  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the  $\text{CO}_2$  bubbles up out of the beverage, releasing the gas into the air (Figure 3). With the lid off the bottle, the  $\text{CO}_2$  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  $\text{CO}_2$  concentration, often referred to as “flat.”

Let us consider the evaporation of bromine as a second example of a system at equilibrium.



An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction.

Figure 4 shows an equilibrium is pictured between liquid bromine,  $\text{Br}_2(l)$ , the dark liquid, and bromine vapor,  $\text{Br}_2(g)$ , the orange gas.



Figure 4. An equilibrium is pictured between liquid bromine,  $\text{Br}_2(l)$ , the dark liquid, and bromine vapor,  $\text{Br}_2(g)$ , the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: <http://images-of-elements.com/bromine.php>)

Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. A sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.

## *Key Concepts and Summary*

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.

## *Exercises*

1. What does it mean to describe a reaction as “reversible”?
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?
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?

### Show Selected Answers

1. The reaction can proceed in both the forward and reverse directions.
3. 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.

5. The concept of equilibrium does not imply equal concentrations, though it is possible.

## Glossary

**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

**reversible reaction:** chemical reaction that can proceed in both the forward and reverse directions under given conditions



## 52. Shifting Equilibria: Le Châtelier's Principle

### *Learning Objectives*

By the end of this module, 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 ( $K$ ). We next 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 perturbation 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  $Q < K$ ) or the reactants (if  $Q > K$ ) 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 1 is the reduction of the equilibrium concentration of  $\text{SCN}^-$  (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  $\text{Fe}(\text{SCN})^{2+}$  should decrease, increasing the concentration of  $\text{SCN}^-$  part way back to its original concentration, and increasing the concentration of  $\text{Fe}^{3+}$  above its initial equilibrium concentration.

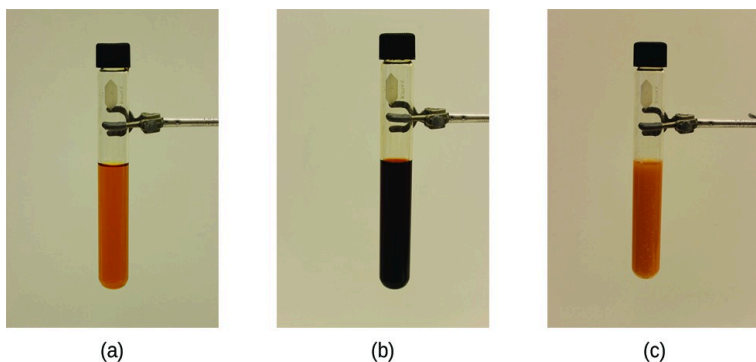
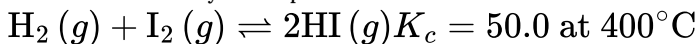


Figure 1. (a) The test tube contains  $0.1 \text{ M Fe}^{3+}$ . (b) Thiocyanate ion has been added to solution in (a), forming the red  $\text{Fe}(\text{SCN})^{2+}$  ion.  $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{Fe}(\text{SCN})^{2+}(\text{aq})$ . (c) Silver nitrate has been added to the solution in (b), precipitating some of the  $\text{SCN}^{-}$  as the white solid  $\text{AgSCN}$ .  $\text{Ag}^{+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{AgSCN}(\text{s})$ . The decrease in the  $\text{SCN}^{-}$  concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the  $\text{Fe}(\text{SCN})^{2+}$ . (credit: modification of work by Mark Ott)

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:



The numeric values for this example have been determined experimentally. A mixture of gases at  $400^\circ\text{C}$  with  $[\text{H}_2] = [\text{I}_2] = 0.221 \text{ M}$  and  $[\text{HI}] = 1.563 \text{ M}$  is at equilibrium; for this mixture,  $Q_c = K_c = 50.0$ . If  $\text{H}_2$  is introduced into the system so quickly that its concentration doubles before it begins to react (new  $[\text{H}_2] = 0.442 \text{ M}$ ), the reaction will shift so that a new equilibrium is reached, at which  $[\text{H}_2] = 0.374 \text{ M}$ ,  $[\text{I}_2] = 0.153 \text{ M}$ , and  $[\text{HI}] = 1.692 \text{ M}$ . This gives:

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c$$

We have stressed this system by introducing additional  $\text{H}_2$ . The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess  $\text{H}_2$ , reducing the amount of uncombined  $\text{I}_2$ , and forming additional  $\text{HI}$ .

## 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.



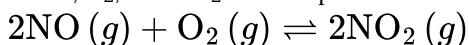
One or more interactive elements has been excluded from this version of the text. You

can view them online here:

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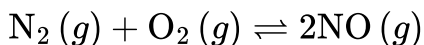
As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Châtelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O<sub>2</sub>, and NO<sub>2</sub> are at equilibrium:



The formation of additional amounts of NO<sub>2</sub> decreases the total number of molecules in the system, because each time two molecules of NO<sub>2</sub> form, a total of three molecules of NO and O<sub>2</sub> 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 favors decomposition of NO<sub>2</sub> into NO and O<sub>2</sub>, which tends to restore the pressure.

Now consider this reaction:



Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

## Effect of Change in Temperature on Equilibrium

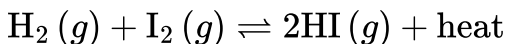
Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we 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.



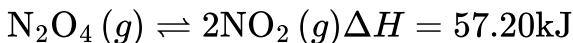
Because this reaction is exothermic, we can write it with heat as a product.



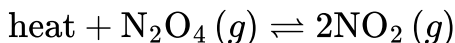
Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of  $\text{H}_2$  and  $\text{I}_2$  and a reduction in the concentration of  $\text{HI}$ . Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors 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  $\text{HI}$  system increases the equilibrium constant: At the new equilibrium the concentration of  $\text{HI}$  has increased and the concentrations of  $\text{H}_2$  and  $\text{I}_2$  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  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in this reaction



The positive  $\Delta H$  value tells us that the reaction is endothermic and could be written



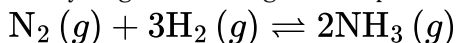
At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown  $\text{NO}_2$  molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless  $\text{N}_2\text{O}_4$  increases, and the concentration of brown  $\text{NO}_2$  decreases, causing the brown color to fade.

This [interactive animation allows you to apply Le Châtelier's principle](#) to predict the effects of changes in concentration, pressure, and temperature on reactant and product concentrations.

## 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



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.

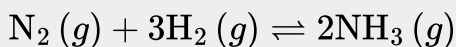
Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

## Fritz Haber

In the early 20th century, German chemist Fritz Haber (Figure 2) 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.



*Figure 2. 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.*



The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen ( $\text{N}_2$ ) 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 Wrocław, 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."<sup>1</sup> Haber defended the use of gas

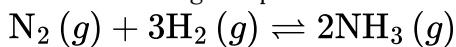
1. Herrlich, P. "The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should

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.

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  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  are at equilibrium or are coming to equilibrium.



The formation of additional amounts of ammonia reduces the

Handle Research That Has the Potential to Create Harm?" *EMBO Reports* 14 (2013): 759–764.

total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  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  $\text{N}_2$  and  $\text{H}_2$ , no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:



Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor 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  $500^\circ\text{C}$ , 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 3).

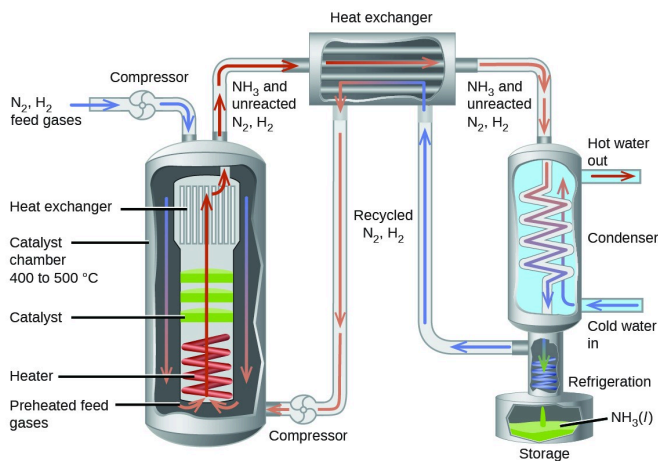


Figure 3. Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

## Key Concepts and Summary

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.

**Table 1. Effects of Disturbances of Equilibrium and K**

<b>Disturbance</b>	<b>Observed Change as Equilibrium is Restored</b>	<b>Direction of Shift</b>	<b>Effect on K</b>
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 fewer 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

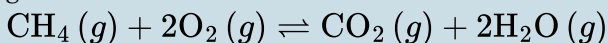
## Exercises

1. The following equation represents a reversible decomposition:



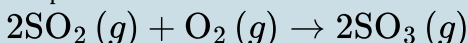
Under what conditions will decomposition in a closed container proceed to completion so that no  $\text{CaCO}_3$  remains?

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?
4. What would happen to the color of the solution in part (b) of Figure 1 if a small amount of  $\text{NaOH}$  were added and  $\text{Fe}(\text{OH})_3$  precipitated? Explain your answer.
5. The following reaction occurs when a burner on a gas stove is lit:



Is an equilibrium among  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  established under these conditions? Explain your answer.

6. A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide,  $\text{SO}_3$ , from sulfur dioxide,  $\text{SO}_2$ , and oxygen,  $\text{O}_2$ , shown below. At high temperatures, the rate of formation of  $\text{SO}_3$  is higher, but the equilibrium amount (concentration or partial pressure) of  $\text{SO}_3$  is lower than it would be at lower temperatures.

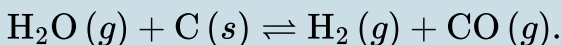


- a. Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
  - b. Is the reaction endothermic or exothermic?
7. Suggest four ways in which the concentration of hydrazine,  $\text{N}_2\text{H}_4$ , could be increased in an equilibrium described by the following equation:  

$$\text{N}_2(g) + 2\text{H}_2(g) \rightleftharpoons \text{N}_2\text{H}_4(g) \Delta H = 95\text{kJ}$$
8. Suggest four ways in which the concentration of  $\text{PH}_3$  could be increased in an equilibrium described by the following equation:  

$$\text{P}_4(g) + 6\text{H}_2(g) \rightleftharpoons 4\text{PH}_3(g) \Delta H = 110.5\text{kJ}$$
9. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?
  - a.  $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g) \Delta H = 92\text{kJ}$
  - b.  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \Delta H = 181\text{kJ}$
  - c.  $2\text{O}_3(g) \rightleftharpoons 3\text{O}_2(g) \Delta H = -285\text{kJ}$
  - d.  $\text{CaO}(s) + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s) \Delta H = -176\text{kJ}$
10. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?
  - a.  $2\text{H}_2\text{O}(g) \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g) \Delta H = 484\text{kJ}$
  - b.  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \Delta H = -92.2\text{kJ}$
  - c.  $2\text{Br}(g) \rightleftharpoons \text{Br}_2(g) \Delta H = -224\text{kJ}$
  - d.  $\text{H}_2(g) + \text{I}_2(s) \rightleftharpoons 2\text{HI}(g) \Delta H = 53\text{kJ}$
11. 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:



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
$$2\text{H}_2 (g) + \text{CO} (g) \rightleftharpoons \text{CH}_3\text{OH} (g) \Delta H = -90.2\text{kJ}$$
  - b. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if more  $\text{H}_2$  is added?
  - c. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CO}$  is removed?
  - d. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CH}_3\text{OH}$  is added?
  - e. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if the temperature of the system is increased?
  - f. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if more catalyst is added?
12. Nitrogen and oxygen react at high temperatures.
- a. Write the expression for the equilibrium constant ( $K_c$ ) for the reversible reaction
$$\text{N}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2\text{NO} (g) \Delta H = 181\text{kJ}$$
  - b. What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if (i) more  $\text{O}_2$  is



- added?
- What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if  $\text{N}_2$  is removed?
  - What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if  $\text{NO}$  is added?
  - What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
  - What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if the temperature of the system is increased?
  - What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if a catalyst is added?
13. Water gas, a mixture of  $\text{H}_2$  and  $\text{CO}$ , is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.
- Write the expression for the equilibrium constant for the reversible reaction  

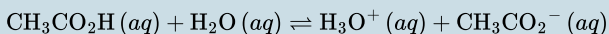
$$\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g) \quad \Delta H = 131.30 \text{ kJ}$$
  - What will happen to the concentration of each reactant and product at equilibrium if more  $\text{C}$  is added?
  - What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2\text{O}$  is removed?
  - What will happen to the concentration of each reactant and product at equilibrium if  $\text{CO}$  is added?
  - What will happen to the concentration of each reactant and product at equilibrium if the

temperature of the system is increased?

14. Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.
- Write the expression for the equilibrium constant ( $K_c$ ) for the reversible reaction  
$$\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \rightleftharpoons 2\text{Fe}(s) + 3\text{H}_2\text{O}(g) \Delta H = 98.7\text{kJ}$$
  - What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
  - What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2\text{O}$  is removed?
  - What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2$  is added?
  - 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?
  - What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?
15. Ammonia is a weak base that reacts with water according to this equation:
- $$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$$
- Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?
- Addition of NaOH

- b. Addition of HCl
- c. Addition of  $\text{NH}_4\text{Cl}$

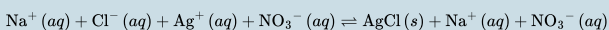
16. Acetic acid is a weak acid that reacts with water according to this equation:



Will any of the following increase the percent of acetic acid that reacts and produces  $\text{CH}_3\text{CO}_2^-$  ion?

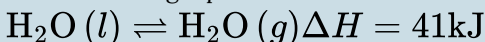
- a. Addition of HCl
- b. Addition of NaOH
- c. Addition of  $\text{NaCH}_3\text{CO}_2$

17. Suggest two ways in which the equilibrium concentration of  $\text{Ag}^+$  can be reduced in a solution of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ag}^+$ , and  $\text{NO}_3^-$ , in contact with solid  $\text{AgCl}$ .

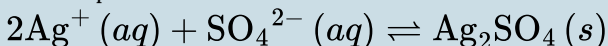


$$\Delta H = -65.9\text{kJ}$$

18. How can the pressure of water vapor be increased in the following equilibrium?



19. 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:



Which of the following will occur?

- a.  $\text{Ag}^+$  or  $\text{SO}_4^{2-}$  concentrations will not change.
- b. The added silver sulfate will dissolve.
- c. Additional silver sulfate will form and precipitate from solution as  $\text{Ag}^+$  ions and

$\text{SO}_4^{2-}$  ions combine.

- d. The  $\text{Ag}^+$  ion concentration will increase and the  $\text{SO}_4^{2-}$  ion concentration will decrease.

Show Selected Answers

1. The amount of  $\text{CaCO}_3$  must be so small that  $P_{\text{CO}_2}$  is less than  $K_p$  when the  $\text{CaCO}_3$  has completely decomposed. In other words, the starting amount of  $\text{CaCO}_3$  cannot completely generate the full  $P_{\text{CO}_2}$  required for equilibrium.

3. 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.

5. 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.

7. Add  $\text{N}_2$ ; add  $\text{H}_2$ ; decrease the container volume; heat the mixture.

9. The change of temperature and pressure have the following results:

- a.  $\Delta T$  increase = shift right,  $\Delta P$  increase = shift left
- b.  $\Delta T$  increase = shift right,  $\Delta P$  increase = no effect
- c.  $\Delta T$  increase = shift left,  $\Delta P$  increase = shift left

d.  $\Delta T$  increase = shift left,  $\Delta P$  increase = shift right

11. The answers are as follows:

- a.  $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2 [\text{CO}]}$
- b.  $[\text{H}_2]$  increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  increases
- c.  $[\text{H}_2]$  increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  decreases
- d.  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  increases
- e.  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  decreases
- f. no changes

13. The answers are as follows:

- a.  $K_c = \frac{[\text{CO}] [\text{H}_2]}{[\text{H}_2\text{O}]}$
- b.  $[\text{H}_2\text{O}]$  no change,  $[\text{CO}]$  no change,  $[\text{H}_2]$  no change
- c.  $[\text{H}_2\text{O}]$  decreases,  $[\text{CO}]$  decreases,  $[\text{H}_2]$  decreases
- d.  $[\text{H}_2\text{O}]$  increases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  decreases
- e.  $[\text{H}_2\text{O}]$  decreases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  increases. In (a), (b), (c), and (d), the mass of carbon will change, but its concentration (activity) will not change.

15. Only (b). In (a), addition of a strong base forces the equilibrium toward forming more  $\text{NH}_3(aq)$ . In (b), the addition of  $\text{HCl}$  causes a reaction with  $\text{NH}_3$  to form more  $\text{NH}_4^+$  by removing  $\text{OH}^-$  as it reacts with the acid to form water. In (c),  $\text{NH}_4^+$  ion causes the equilibrium to shift to the left, forming more  $\text{NH}_3(aq)$ .

17. Add  $\text{NaCl}$  or some other salt that produces  $\text{Cl}^-$  to the solution. Cooling the solution forces the equilibrium to the right, precipitating more  $\text{AgCl}(s)$ .

19. (a) The solution already holds as many ions as it can.

The amino acid alanine has two isomers,  $\alpha$ -alanine and  $\beta$ -alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of  $\alpha$ -alanine freezes at the lowest temperature. Which form,  $\alpha$ -alanine or  $\beta$ -alanine, has the larger equilibrium constant for ionization ( $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$ )?

The freezing-point depression is proportional to the number of particles produced in a solvent. For a weak electrolyte,  $\Delta T = i k_f m$ , where  $i$  is the number of ions produced from a solute. Because both isomers have identical molecular masses and are dissolved in the same amount of solvent,  $k_f$  and  $m$  are constants. Any difference in the reduction of the freezing point must, therefore, reflect a difference in the degree of ionization,  $i$ , of the two forms of alanine into fragments—namely, a proton and the anion. A greater number of ions will be produced by the form with the larger equilibrium constant, which results in a lower freezing point for that species. Since  $\alpha$ -alanine has a lower freezing point and, consequently, the larger freezing-point depression, it must have the larger number of ions in solution and has the larger value of  $K_c$ .

## Glossary

**Le Châtelier's principle:** when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

**position of equilibrium:** concentrations or partial pressures of

components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

**stress:** change to a reaction's conditions that may cause a shift in the equilibrium

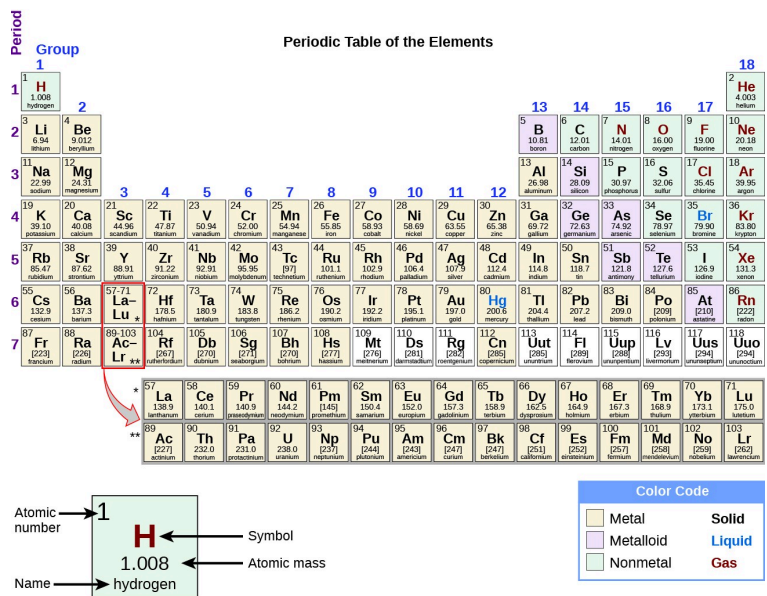




PART XV  
APPENDICES



# 53. The Periodic Table



# 54. Units and Conversion Factors

## Units of Length

### Metric System

- 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)

### US System

- angstrom ( $\text{\AA}$ ) =  $10^{-8}$  cm (exact, definition) =  $10^{-10}$  m (exact, definition)
- inch (in.) = 2.54 cm (exact, definition)
- yard (yd) = 0.9144 m
- mile (US) = 1.60934 km

## Units of Volume

### Metric System

- liter (L) = 0.001 m<sup>3</sup> (exact, definition) = 1000 cm<sup>3</sup> (exact, definition) = 1.057 (US) quarts
- milliliter (mL) = 0.001 L (exact, definition) = 1 cm<sup>3</sup> (exact, definition)
- microliter ( $\mu\text{L}$ ) = 10<sup>-6</sup> L (exact, definition) = 10<sup>-3</sup> cm<sup>3</sup> (exact, definition)

### US System

- 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

## Units of Mass

### Metric System

- 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

## US System

- 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

## Units of Energy

- 4.184 joule (J) = 1 thermochemical calorie (cal)
- 1 thermochemical calorie (cal) =  $4.184 \times 10^7 \text{ erg}$
- erg =  $10^{-7} \text{ J}$  (exact, definition)
- electron-volt (eV)  
=  $1.60218 \times 10^{-19} \text{ J} = 23.061 \text{ kcal mol}^{-1}$
- liter-atmosphere = 24.217 cal = 101.325 J (exact, definition)
- nutritional calorie (Cal) = 1000 cal (exact, definition) = 4184 J
- British thermal unit (BTU) =  $1054.804 \text{ J}^1$

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.

## Units of Pressure

- torr = 1 mm Hg (exact, definition)
- pascal (Pa) =  $\text{N m}^{-2}$  (exact, definition) =  $\text{kg m}^{-1} \text{s}^{-2}$  (exact, definition)
- atmosphere (atm) = 760 mm Hg (exact, definition) = 760 torr (exact, definition) =  $101,325 \text{ N m}^{-2}$  (exact, definition) = 101,325 Pa (exact, definition)
- bar =  $10^5 \text{ Pa}$  (exact, definition) =  $10^5 \text{ kg m}^{-1} \text{s}^{-2}$  (exact, definition)

# 55. Fundamental Physical Constants



Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27} \text{ kg}$
Avogadro's number	$6.0221367 \times 10^{23} \text{ mol}^{-1}$
Boltzmann's constant ( $k$ )	$1.380658 \times 10^{-23} \text{ J K}^{-1}$
charge-to-mass ratio for electron ( $e/m_e$ )	$1.75881962 \times 10^{11} \text{ C kg}^{-1}$
electron charge ( $e$ )	$1.60217733 \times 10^{-19} \text{ C}$
electron rest mass ( $m_e$ )	$9.1093897 \times 10^{-31} \text{ kg}$
Faraday's constant ( $F$ )	$9.6485309 \times 10^4 \text{ C mol}^{-1}$
gas constant ( $R$ )	$8.205784 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$
molar volume of an ideal gas, 1 atm, 0 °C	$22.41409 \text{ L mol}^{-1}$
molar volume of an ideal gas, 1 bar, 0 °C	$22.71108 \text{ L mol}^{-1}$
neutron rest mass ( $m_n$ )	$1.6749274 \times 10^{-27} \text{ kg}$
Planck's constant ( $h$ )	$6.6260755 \times 10^{-34} \text{ J s}$
proton rest mass ( $m_p$ )	$1.6726231 \times 10^{-27} \text{ kg}$
Rydberg constant ( $R$ )	$1.0973731534 \times 10^7 \text{ m}^{-1} = 2.1798736 \times 10^{-18} \text{ J}$
speed of light (in vacuum) ( $c$ )	$2.99792458 \times 10^8 \text{ m s}^{-1}$