CHEMISTRY: PHYSICAL PRINCIPLES



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Chemistry: Physical Principles

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Guide to Using the Textbook

Purpose of This Guide

The CHM 135H OER textbook is more than a collection of information to read. It includes learning objectives, explanations, worked examples, practice problems, summaries, and review materials that can support different stages of your learning.

This guide explains how to use these features effectively throughout the course. It also introduces practical strategies for learning chemistry, solving problems, and moving forward when you get stuck.

The Approach Behind the Textbook

Chemistry is best learned through active engagement. Reading can be an important starting point, but developing a strong understanding requires you to apply ideas, work through problems, explain your reasoning, and identify what you still need to review.

The textbook is organized around several principles:

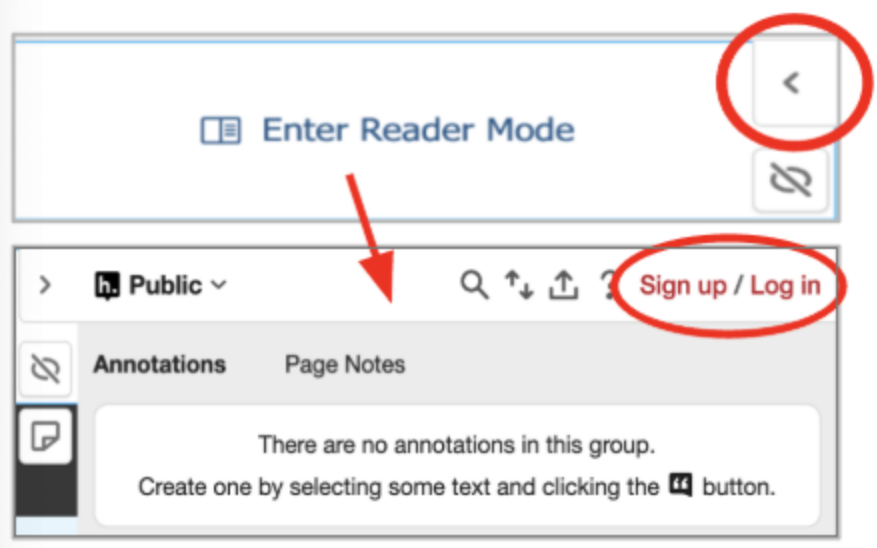
- Practice problems are an essential part of learning chemistry.
- Worked examples demonstrate how chemical problems can be approached.
- Learning objectives help you identify what you should be able to understand or do.
- Summaries and glossaries support review, but they do not replace detailed learning and practice.
- Complete solutions allow you to evaluate your reasoning after making an independent attempt.
- Regular engagement with the textbook is more effective than reading large amounts immediately before a test.

The textbook is ultimately intended to help you become a more independent learner. As you progress through the course, you should become better at identifying what a question is asking, choosing an appropriate strategy, evaluating whether your answer makes sense, and recognizing when you need to review a concept of seek additional help.

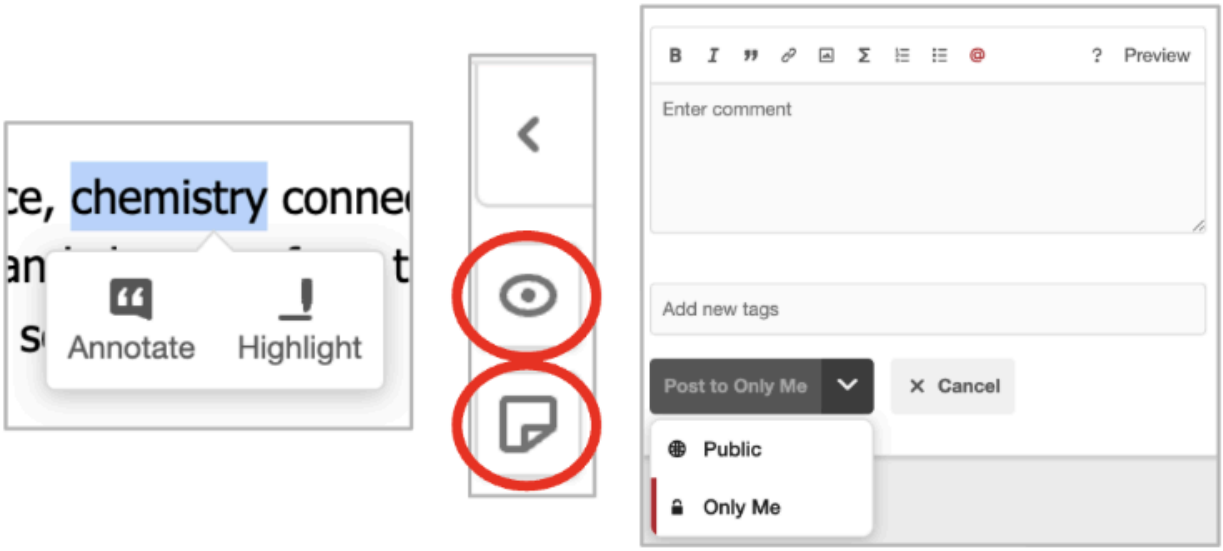
Accessing and Navigating the Textbook

Getting Started

This textbook is free and can be accessed without an account. To annotate, highlight, or bookmark pages, you will need to create a free Hypothesis account using your student email. Hypothesis is a web annotation tool that can be accessed by clicking the small arrow in the upper right corner of the page. A sidebar will appear with the option to sign up or log in and guide you through the short account-creation process.



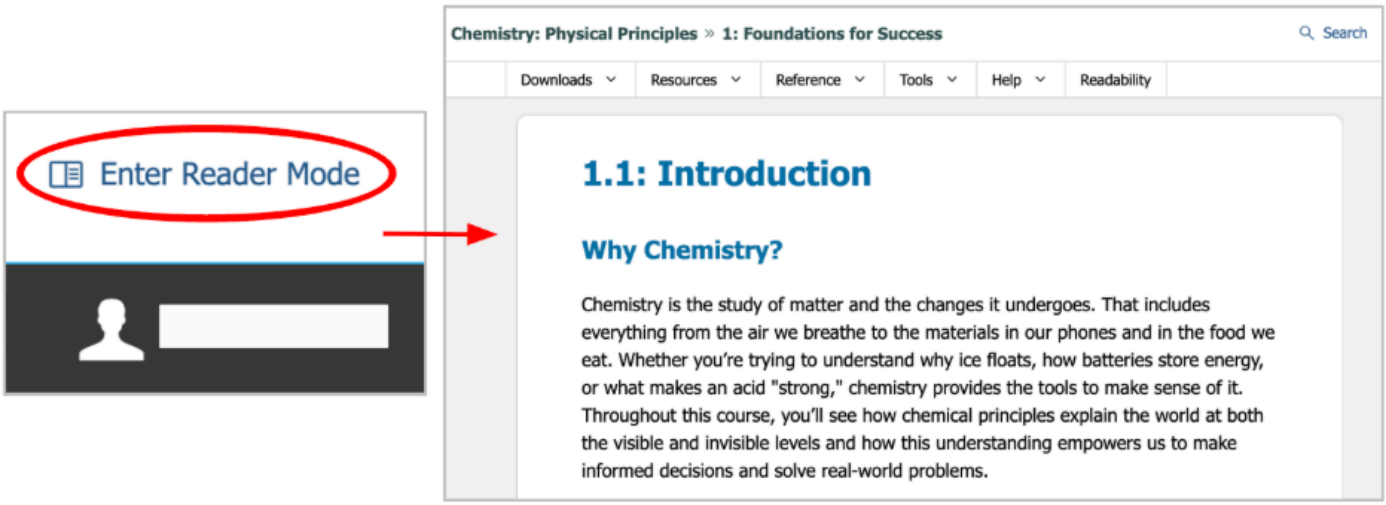
Once logged in, text can be annotated and highlighted by interacting with the same sidebar arrow as before or by highlighting the text with your cursor. Annotations can be made public or private, and you can join groups of other users. Highlights are only visible to you and can be toggled on and off with the eye symbol below the sidebar arrow in in the upper right-hand corner. Below the eye is a page symbol, which can be used to make general page notes that can be public or private.



As the textbook exists as an online website, it can be accessed with any device connected to the internet. However, there are ways to use it offline, as discussed later.

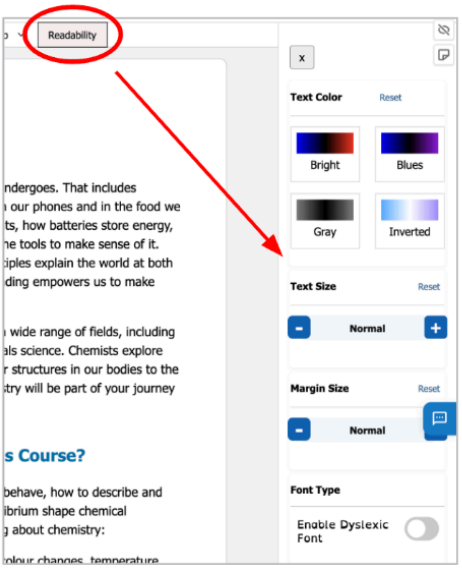
Reader Mode & Readability

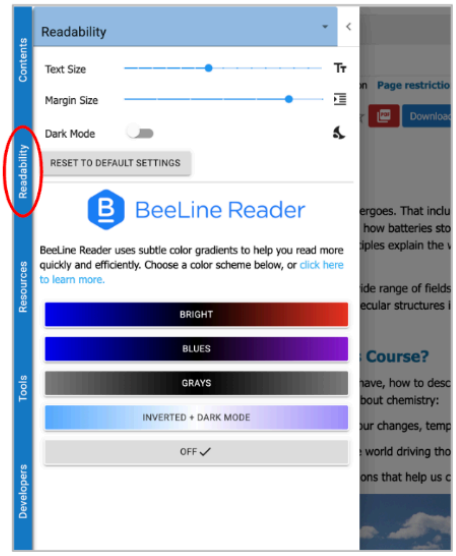
The textbook is designed to be easy to read in its standard form. You can also use Reader Mode to simplify the page and reduce visual clutter. To turn on Reader Mode, click the book icon labelled “Enter Reader Mode” below it. This will change the appearance of the textbook, while maintaining access to the annotation and highlighting tools in the sidebar.



Because Reader Mode centers the text and takes up less space on the webpage, it is recommended to only use Reader Mode on devices wide enough to properly display the text; phones or devices of similar size are not recommended unless the margins are adjusted (discussed below).

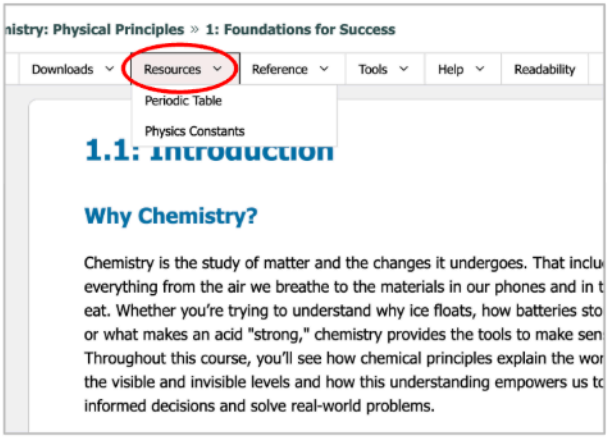
Both the regular page and Reader Mode have a toolbar to access content, tools, and extra support. In Reader Mode, this appears as dropdown bars near the top of the page. In standard view, it appears as a vertical blue bar on the left side of the screen. In both modes, the “Readability” options allow you to adjust accessibility features, such as changing the text color, text size, and size of the margins. Dark Mode is available under “Readability” in the standard view, while Reader Mode included an option for a dyslexic-friendly font. (Please note that while Dark Mode is toggled on the standard view, Reader Mode will not function.)

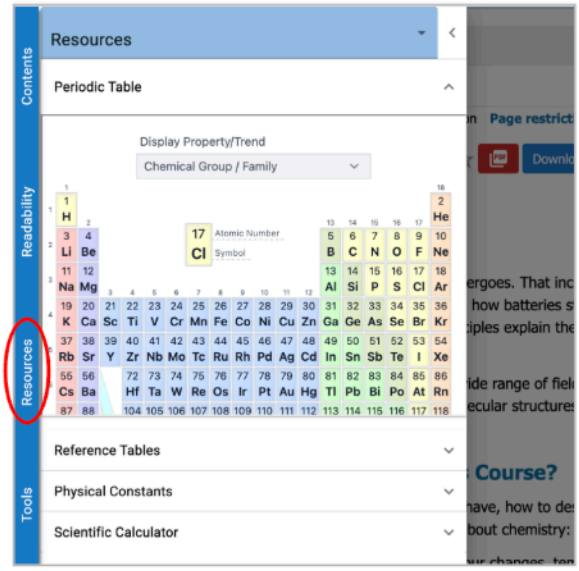




The “Resources” tab in standard view provides a periodic table, reference tables, physical constants, and a scientific calculator to use as you follow the content. While in Reader Mode, the “Resources” tab contains the periodic table and useful constants.

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Finding Information

The Chemistry: Physical Principles home page contains fourteen boxes that will bring you to different sections of the textbook. The non-content portions include the Front Matter, Reference, and Back Matter, all of which are useful for navigating the textbook.

The Front Matter contains a Table of Contents, which lists the names of, and links to, each chapter, as well links to the Reference and Back Matter sections. There are eleven content chapters, which are split into pages that also have their own links.



When in full screen, each page will have blue arrow symbols on the left and right sides of the screen that can be used to navigate to the previous or next page, both in and out of Reader Mode. Otherwise, links can be found at the top and bottom of each page. The textbook contains hyperlinks that connect related parts of the book. For example, in the end-of-chapter problems, each section of problems links back to the corresponding section of the chapter.

By default, clicking a hyperlink will open the linked page in the current tab. If you want to keep your place in the textbook, right-click the link and select “Open Link in New Tab.” The links found in cited references listed at the bottom of a content page will open in a new tab.

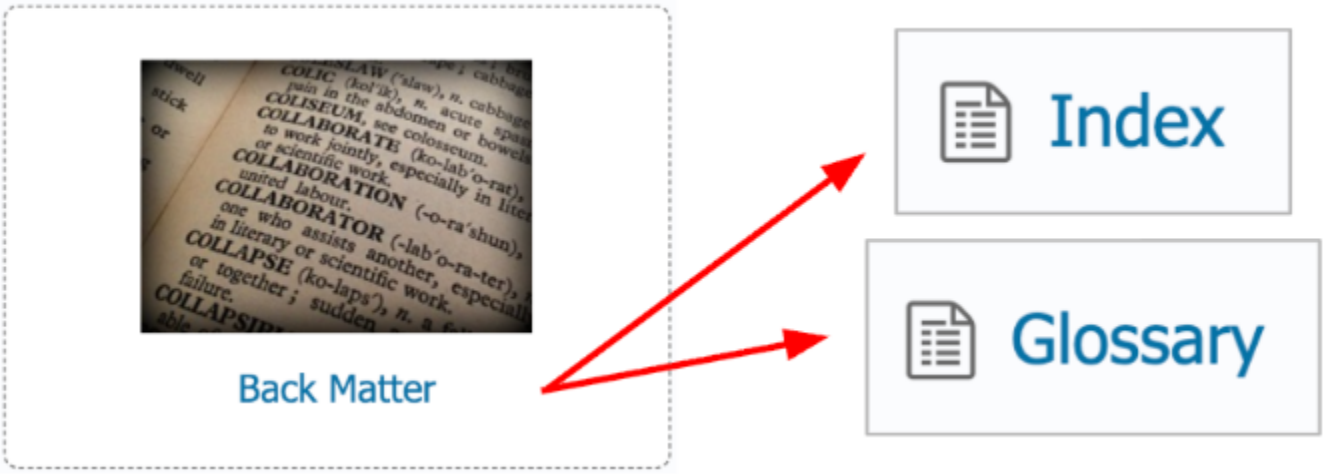
Why Chemistry?

Chemistry is the study of matter and the changes it undergoes. That includes everything from the air we breathe to the materials in our phones and in the food we eat. Whether you're trying to understand why ice floats, how batteries store energy, or what makes an acid "strong," chemistry provides the tools to make sense of it. Throughout this course, you'll see how chemical principles explain the world at both the visible and invisible levels and how this understanding empowers us to make informed decisions and solve real-world problems.

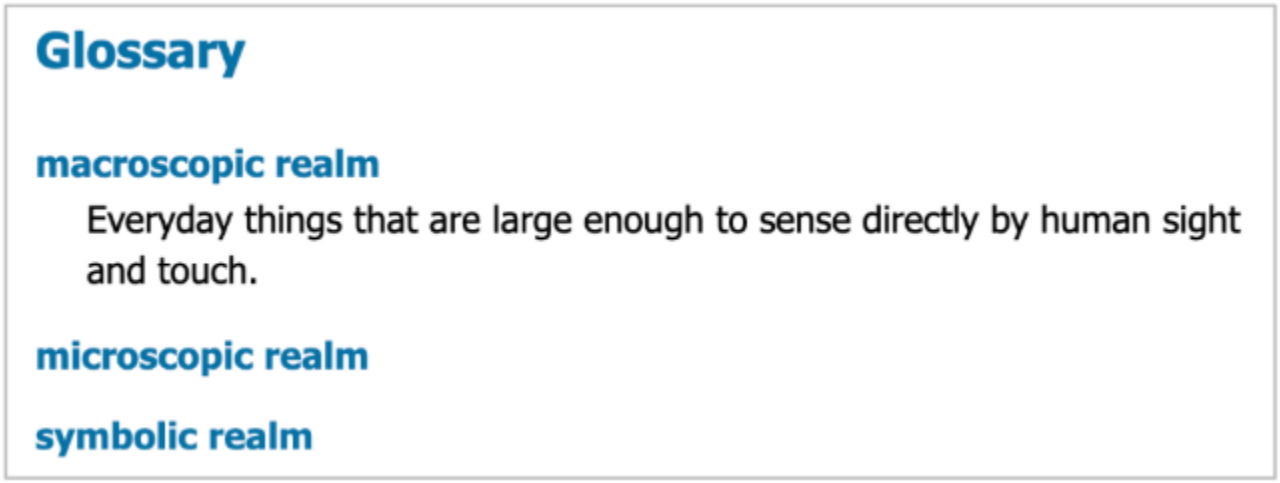
Often called the central science, chemistry connects a wide range of fields, including biology, medicine, environmental science, and materials science. Chemists explore how matter behaves and changes, from the molecular structures in our bodies to the reactions that power batteries or purify water. Chemistry will be part of your journey in most areas of science.

1: Foundations for Success

The Back Matter contains the Index and Glossary, the former listing important terms with links to the chapter in which they first appear, and the latter providing the definition of every notable term introduced in the textbook.



Each page of content also has its own glossary at the bottom, with blue words that can be clicked on to reveal their definition.

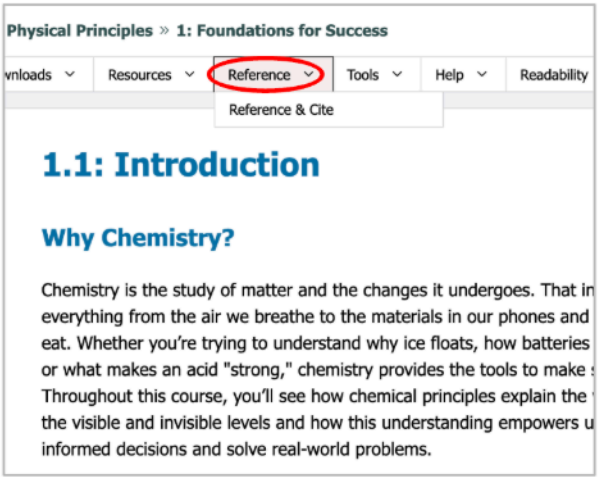


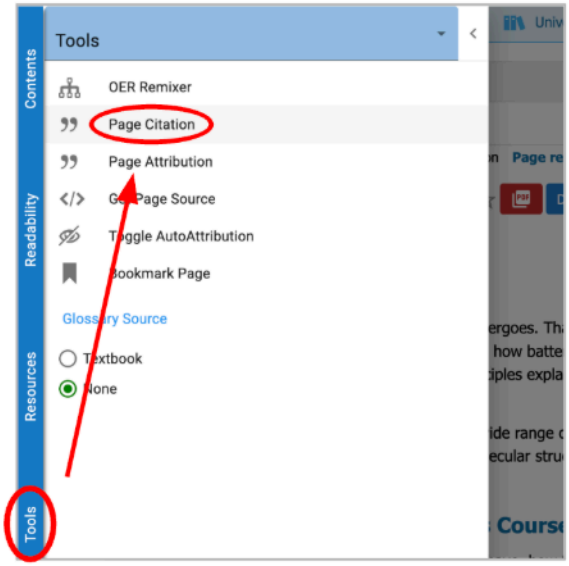
The Reference section contains links to tables with mathematical and chemical constants, common equations, and the periodic

table. It also has a section on green chemistry and its principles, which introduces the growing awareness of environmental chemical impact and sustainable steps that we, as chemists, can take to mitigate these effects.

Citing the Textbook

This textbook may be cited as a source, but please keep in mind that it does not count as a peer-reviewed journal. ACS format, along with other citation styles, can be found under the “Reference” tab at the top of a page while in Reader Mode, and under “Tools” in the regular page sidebar. Be sure to include the date the page was accessed.

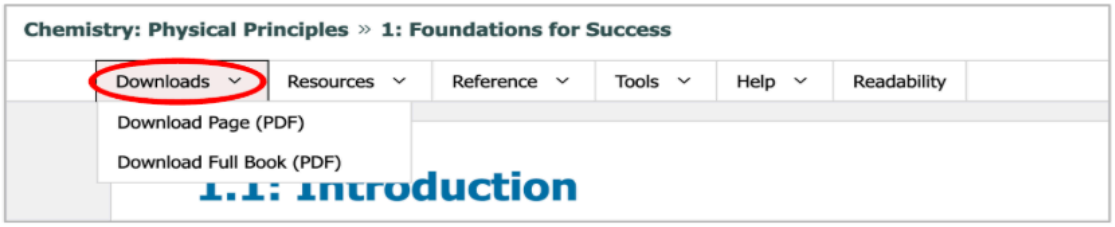


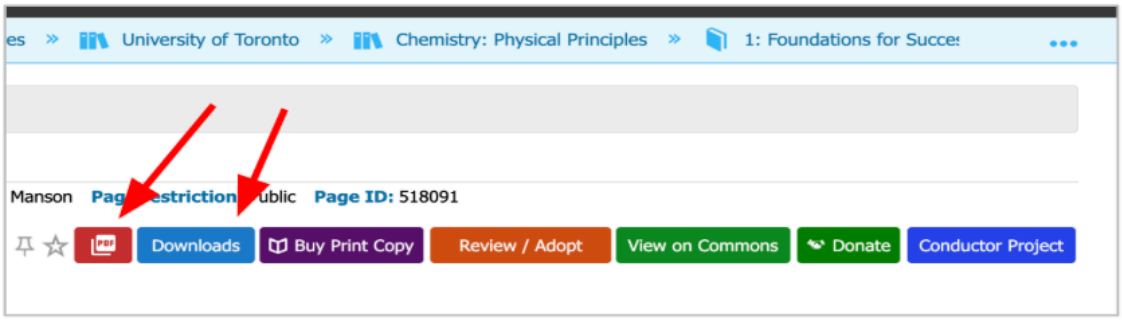


Working Offline

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Please note that if there are any changes made to the textbook, such as fixed typos, older downloaded versions will not reflect these changes.





Note that any links within PDF versions of the textbook will bring you back to the online webpage. Additionally, take care when completing practice problems within the PDF version, as answers will be automatically visible – it is strongly recommended that you use the online version to access the end-of-chapter problems. Certain interactive features may not be available, such as the page glossaries, and the full glossary is only available on the website.

Learning Effectively with the Textbook

Learning Features

The textbook contains several recurring learning features. Each serves a different purpose and can be used at different stages of learning.

As you work through examples and practice problems, focus on understanding the chemistry and developing problem-solving skills rather than memorizing a set of steps. Ask yourself why a particular approach works, how you know which principles or equations are relevant, and how you would adapt the approach if the problem were changed. The goal is to develop strategies that you can apply to new problems, not simply to reproduce the solution to a familiar one.

Learning Objectives

Learning objectives identify the knowledge and skills addressed in a section. Read them before beginning a section to understand what you are expected to learn. Return to the objectives later to check if you can explain or demonstrate each objective referring to textbook.

Worked Examples

Worked examples demonstrate how to approach a particular type of problem. Pay attention not only to the calculations, but also to **why** each step is taken and how the approach could be applied to a similar problem.

Practice Problems

Practice problems allow you to test whether you can apply the concepts independently. Try each problem before looking at hints or solutions and show your reasoning as you work. This makes it easier to identify where you are having difficulty and what you need to review.

Chapter Summaries

Chapter summaries provide an overview of the major concepts covered in a chapter. They can be used for previewing material before class or organize your review afterward. However, summaries are not intended to replace reading relevant sections,

reviewing lecture material, or solving practice problems.

The Glossary

The glossary provides quick definitions of important terms. Use it when you encounter unfamiliar vocabulary or need to review terminology before a quiz, test, or lecture. Knowing a definition is only the first step. You should also be able to explain the concept in your own words and apply it in context.

There are also small glossaries at the bottom of each page that provide the definitions for important terms used on that page. Note that if a term has been used and defined in a previous chapter, it will not appear again in a mini glossary.

End-of-Chapter Questions

End-of-chapter questions help you bring together ideas from across a chapter. Use them after reviewing the individual sections toto test your overall understanding and identify areas that need more review.

Complete Solutions

Complete solutions allow you to compare your reasoning with a correct approach. Make a genuine attempt at each problem before looking at the solution. Solutions are immediately visible in the PDF version of the textbook, so it's recommended to use the online version for problem-solving. At a minimum, take care not to read the solutions before attempting the question yourself.

Chemistry of Everyday Life & Green Connections

The "Chemistry of Everyday Life" and "Green Connections" boxes provide additional context and applications. Unless your instructor indicates otherwise, students are not responsible for the content in these boxes for course assessments.

Using the Textbook Before Class

You do not need to master the entire topic before attending a lecture. The goal of preparation is to become familiar with the language and main ideas so that the lecture is easier to follow.

Before class, you might:

- Read the learning objectives.
- Skim the section headings.
- Read the chapter or section summary.
- Review unfamiliar vocabulary in the glossary.
- Look over one or two worked examples.
- Make note of concepts or terms that seem unclear.

Even a brief preview can make it easier to recognize important ideas during the lecture.

Using the Textbook After Class

After class, use the textbook to strengthen and test your understanding.

A useful sequence is:

1. Review your lecture notes and identify any concepts that remain unclear.
2. Read the relevant textbook sections.

3. Study the related worked examples.
4. Attempt practice problems without looking at the solutions.
5. Review your answers and identify any gaps in your reasoning.
6. Revisit the relevant concepts or ask for help when needed.

Course supports such as tutorials, peer tutoring, office hours, teaching assistants, and instructors are most helpful when used regularly rather than only immediately before an assessment.

Making the Most of Practice Problems

Solving problems is one of the most important parts of learning chemistry. Reading an explanation or following a completed solution can create a sense of familiarity, but familiarity is not the same as being able to solve a problem independently. If you spend more time reading solutions than solving problems yourself, you may end up memorizing steps without understanding the chemistry behind them. Working through problems yourself helps you understand not only what to do, but why you are doing it and how to adapt your approach to a new problem.

To use practice problems effectively:

- Attempt the problem before viewing the solution.
- Work on paper instead of trying to complete every step mentally.
- Write down the information provided and identify what the problem is asking.
- Show equations, units, assumptions, and intermediate steps.
- Explain why you are using a particular formula or principle.
- Check whether your final answer is reasonable.
- Keep track of mistakes that you make repeatedly and look for patterns in them
- If you get stuck, identify where your reasoning breaks down, ask for help if needed, and then try the problem again on your own.

What to Do if You Get Stuck

Getting stuck is a normal part of learning chemistry. It often means that you have reached the point where deeper learning can occur.

When you are unsure how to continue:

1. Identify what the problem is asking you to determine.
2. Write down the information provided.
3. Identify the concept or chapter connected to the problem.
4. Review the relevant textbook section, class notes, or a similar worked example.

Use what you have reviewed to attempt the problem again without copying the example. If you are still stuck, ask a teaching assistant, instructor, tutor, or classmate for help.

When asking for help, bring your written attempt and explain where you became stuck. This makes it easier to identify and address the specific part of your reasoning that needs attention.

Understanding the Problem-Difficulty Ratings

The end-of-chapter practice problems are assigned a difficulty rating. The rating reflects the complexity of the reasoning required, not the length of the calculation.

★ **One Star:** Routine application of a single concept or procedure.

★★ **Two Stars:** Requires an additional step or combines ideas in a less familiar way.

★★★ **Three Stars:** Requires integrating multiple concepts and deciding how to approach the problem.

A problem with more stars is not necessarily longer or more difficult because it involves more calculations. The challenge may instead come from deciding which information is relevant, identifying the concepts that apply, or developing a solution strategy.

When beginning a new topic, you may wish to start with one-star problems and gradually progress to more challenging questions. As you develop your understanding, practice problems at all three levels.

Common Study Mistakes

Here are some common study habits we see in CHM 135H, along with advice for more effective learning.

Instead of reading a solution before attempting the problem:

Make an independent attempt first, even when you are not certain how to begin.

Instead of highlighting large portions of the textbook:

Write brief notes in your own words, identify the central idea, or create a question that tests the material.

Instead of reading an entire chapter immediately before a test:

Space your studying over several shorter sessions and return to the material regularly.

Instead of spending too much time on the easier problems:

Use a combination of routine, multi-step, and challenging problems to increase your understanding and problem-solving skills

Instead of immediately checking whether your answer is correct:

Review your reasoning first and ask whether the answer is chemically and mathematically reasonable.

Instead of memorizing a sequence of steps without understanding it:

Ask why each step is appropriate and under what conditions the strategy can be used.

A Learning Cycle

Learning chemistry is not a linear process. You may move back and forth between encountering new ideas, making sense of them, practicing, and checking your understanding. For example, attempting a problem may reveal that you need to return to a concept and work on your understanding before trying the problem again.

Encounter: See new ideas through lectures, the textbook, worked examples, or other course materials.

Make Sense: Connect new ideas to what you already know. Read explanations, work through examples, ask questions, and seek help when something doesn't make sense.

Practice: Apply what you have learned by solving problems independently and explaining your reasoning.

Check: Compare your reasoning with solutions, identify mistakes or gaps in your understanding, and determine what you need to

work on next.

Revisit: Return to concepts and problems after some time has passed. Repeatedly working with material helps strengthen your understanding and ability to apply it.

Regularly moving through these stages, and returning to earlier stages when needed, is more effective than relying on rereading or intensive studying immediately before a test.

Learning chemistry takes time and practice. You will not understand everything the first time you encounter it, and getting stuck is a normal part of the process. Use the textbook actively, learn from your mistakes, and seek help when you need it. The goal is not to know everything immediately, but to keep building your understanding and your ability to solve new problems.

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1: FOUNDATIONS FOR SUCCESS

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1.2: Units and Measurements

1.3: Atoms, Elements, and the Mole

1.4: Compounds and How We Represent Them

1.5: Chemical Reactions and Equations

1.6: Reaction Stoichiometry

1.7: Molarity and Solution Stoichiometry

1.8: Useful Math Functions in Chemistry

1.E: Foundations for Success (Exercises)

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1.1: Introduction

Why Chemistry?

Chemistry is the study of matter and the changes it undergoes. That includes everything from the air we breathe to the materials in our phones and in the food we eat. Whether you're trying to understand why ice floats, how batteries store energy, or what makes an acid "strong," chemistry provides the tools to make sense of it. Throughout this course, you'll see how chemical principles explain the world at both the visible and invisible levels and how this understanding empowers us to make informed decisions and solve real-world problems.

Often called the central science, chemistry connects a wide range of fields, including biology, medicine, environmental science, and materials science. Chemists explore how matter behaves and changes, from the molecular structures in our bodies to the reactions that power batteries or purify water. Chemistry will be part of your journey in most areas of science.

What Chemistry Will You See in This Course?

In this course, you'll learn how atoms and molecules behave, how to describe and predict chemical reactions, and how energy and equilibrium shape chemical processes. We'll move between three ways of thinking about chemistry:

Macroscopic: what you can see or measure (e.g., colour changes, temperature, gas volume)

Microscopic: atoms, molecules, and ions (the invisible world driving those changes)

Symbolic: chemical formulas, equations, and calculations that help us connect the two

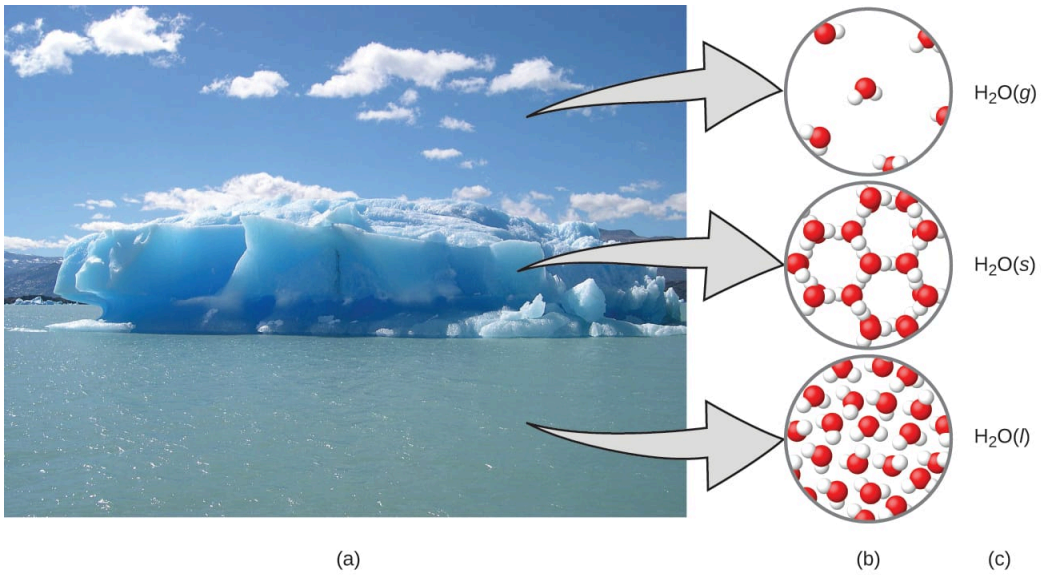


Figure 1.1.1: (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (*g*), (s), and (*l*) symbolize its phases. (credit a: modification of work by "Gorkaazk"/Wikimedia Commons)

How to Use This Chapter

This chapter reviews key high school chemistry topics that you'll need throughout the course. Not everyone will need to spend the same amount of time here. If you're confident in your chemistry background, skim through the chapter and try the end-of-chapter problems first. If you get stuck, go back to the relevant section for a refresher. If chemistry feels new or challenging, work through

the sections in order. Each one builds on the last, with examples and practice to help you gain confidence.

Glossary

macroscopic realm
: Everyday things that are large enough to sense directly by human sight and touch.

microscopic realm
: Things that are much too small to be sensed directly.

symbolic realm
: Specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

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1.2: Units and Measurements

Learning Objectives

- Identify and use common SI base units, prefixes, and derived units such as volume and density.
- Convert between units using dimensional analysis and appropriate conversion factors.
- Express measurements in scientific notation and determine the correct number of significant figures.
- Apply significant figure rules in calculations involving multiplication, division, addition, and subtraction.

In chemistry, we describe the world using measurements. Each measurement consists of two essential components:

- A number, which indicates the magnitude
- A unit, which specifies what is being measured (such as grams, litres, or seconds)

Both components are necessary. For example, stating that "the mass is 25" is ambiguous unless a unit, such as grams or kilograms, is provided.

Common SI Units in Chemistry

Chemists use the International System of Units (SI units), which is based on standardized definitions. The table below lists some units commonly used in chemistry:

Quantity	Unit	Symbol
Mass	kilogram	kg
Length	meter	m
Temperature	kelvin	K
Amount of substance	mole	mol
Time	second	s
Energy	joule	J

Note: Temperature in chemistry is usually expressed in either degrees Celsius (°C) or kelvin (K). These two units are related by:

$$T_k = T_C + 273.15$$

Unit Prefixes

Many measurements in chemistry involve very large or very small numbers. To make these easier to work with, SI units use prefixes that represent powers of ten. Here are some commonly used prefixes:

Prefix	Symbol	Meaning	Example
kilo	k	10^3	1 km = 1000 m
centi	c	10^{-2}	1 cm = 0.01 m
milli	m	10^{-3}	1 mL = 0.001 L
micro	µ	10^{-6}	1 µL = 0.000001 L
nano	n	10^{-9}	1 ng = 0.000000001 g

Scientific Notation

Chemists often work with numbers that are either very large or very small. Scientific notation is a convenient way to express such values:

- 3.2×10^{4} represents 32 000
- 4.5×10^{-6} represents 0.0000045

This notation simplifies calculations and improves clarity in written work.

Derived SI Units

Many units used in chemistry are derived from the seven SI base units. For example, we use the base unit of length to define volume, and the base units of mass and volume to define density.

Volume

Volume is the measure of the amount of space an object occupies. It can be calculated using:

Volume = length × width × height

The standard SI unit of volume is the cubic meter (m^3), but this is often too large for laboratory use (Figure 1.2.1). Commonly used units include:

- 1 liter (L) = 1 cubic decimeter (1 dm^3)
- 1 milliliter (mL) = 1 cubic centimeter (1 cm^3)

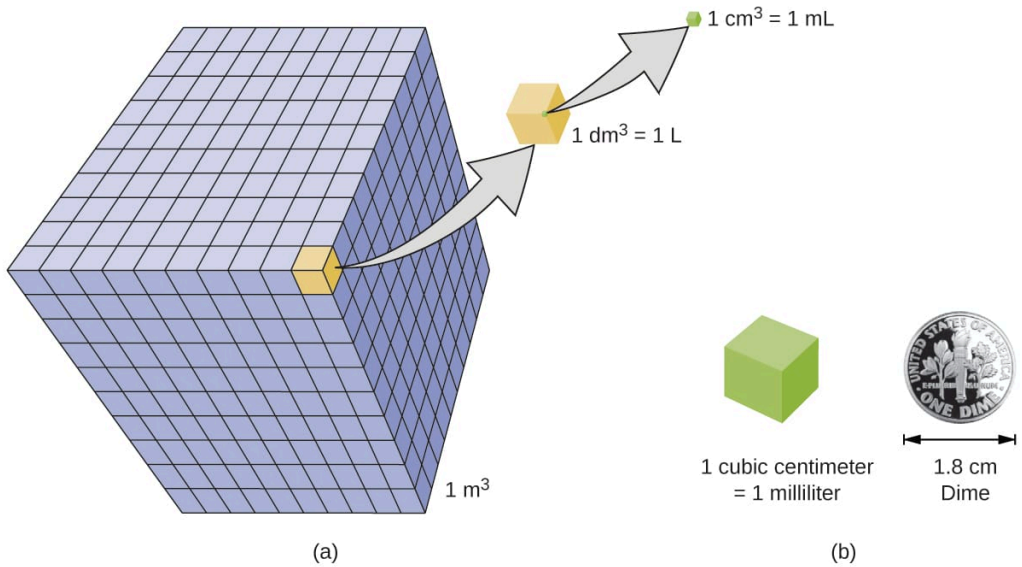


Figure 1.2.1: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Density

Density is the ratio of the mass of a substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3), but more convenient units are often used:

- g/cm^3 for solids and liquids

- g/L for gases.

Although there are exceptions, most solids and liquids have densities between about 0.7 g/cm^3 (gasoline) and 19 g/cm^3 (gold). Air has a density of approximately 1.2 g/L. Density is useful for identifying substances and for converting between mass and volume. The density is calculated by dividing mass by volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.2.1}$$

Example 1.2.1: Calculation of Density

Gold, in bricks, bars, and coins, has been a form of currency for centuries. To trick people into paying for 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. Although lead is a dense substance, it is not as dense as gold (19.3 g/cm^3) and the mass of the brick would give the trick away. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume.

The volume of a cube is calculated by cubing the edge length:

$$V = l^3 = (2.00\ \text{cm})^3 = 8.00\ \text{cm}^3$$

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

(We will discuss the rules for significant figures in the next section.)

Exercise 1.2.1

a) What is the volume (cm^3) of a cube with an edge length of 0.843 cm?

b) If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper?

Answer available at the end of this section.

Unit Conversions

Calculations in chemistry often involve converting between different units, for example, from millilitres to litres or from grams to kilograms. To do this, we use conversion factors, which are ratios that relate one unit to another.

A conversion factor is a fraction that equals 1, such as:

$$\left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) \quad \text{or} \quad \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)$$

The ratio equals 1 because 1000 mL = 1 L. Multiplying by it does not change the value, only the units. You choose the version that cancels the unwanted unit, leaving the unit you want.

This method of unit conversion is called dimensional analysis (also known as the factor-label method). It works by multiplying the starting value by one or more conversion factors, cancelling units like algebraic variables until only the desired unit remains.

For example, let's convert 2.5 h to seconds. This involves two conversion factors:

1 h = 60 min, 1 min = 60 s.

$$2.5 \cancel{\text{ h}} \left(\frac{60 \cancel{\text{ min}}}{1 \cancel{\text{ h}}} \right) \left(\frac{60 \text{ s}}{1 \cancel{\text{ min}}} \right) = 9000 \text{ s}$$

Example 1.2.2

A hummingbird flies at 14.7 m/s. Calculate its speed in km/h.

Solution

Convert metres to kilometres and seconds to hours:

$$14.7 \frac{\cancel{\text{m}}}{\cancel{\text{s}}} \left(\frac{\text{km}}{1000 \cancel{\text{m}}} \right) \left(\frac{60 \cancel{\text{ s}}}{1 \cancel{\text{ min}}} \right) \left(\frac{60 \cancel{\text{ min}}}{1 \text{ h}} \right) = 52.9 \text{ km/h}$$

Exercise 1.2.2

Bamboo is a fast-growing plant and can grow up to 91 cm/day. What is this growth rate in mm/min?

Answer available at the end of this section.

Example 1.2.3

Convert 5.2 mm^3 to mL.

Solution

Conversion factors:

1 cm = 10 mm; so 1 cm^3 = (10 mm)^3 = 1000 mm^3

1 mL = 1 cm^3

Convert mm^3 to cm^3 and then to mL:

$$5.2 \cancel{\text{ mm}^3} \left(\frac{1 \text{ cm}^3}{10^3 \cancel{\text{ mm}^3}} \right) \left(\frac{1 \text{ mL}}{1 \cancel{\text{ cm}^3}} \right) = 0.0052 \text{ mL}$$

Exercise 1.2.3

Convert 0.038 mL to mm^3.

Answer available at the end of this section.

Significant Figures in Measurement

Some numbers in science are exact. For example, if you count 12 eggs in a carton, there is no uncertainty; you have exactly 12 eggs. Defined quantities are also exact: 1 meter is exactly 100 centimeters, and 1 kilogram is exactly 1000 grams. Most measurements in science are not exact. They always involve some uncertainty because of the limitations of the measuring tool and how we read it.

Let's say you're measuring a liquid in a graduated cylinder (Figure 1.2.2). You read the volume at the bottom of the meniscus, the

curved surface of the liquid, and estimate its position between the marked lines.

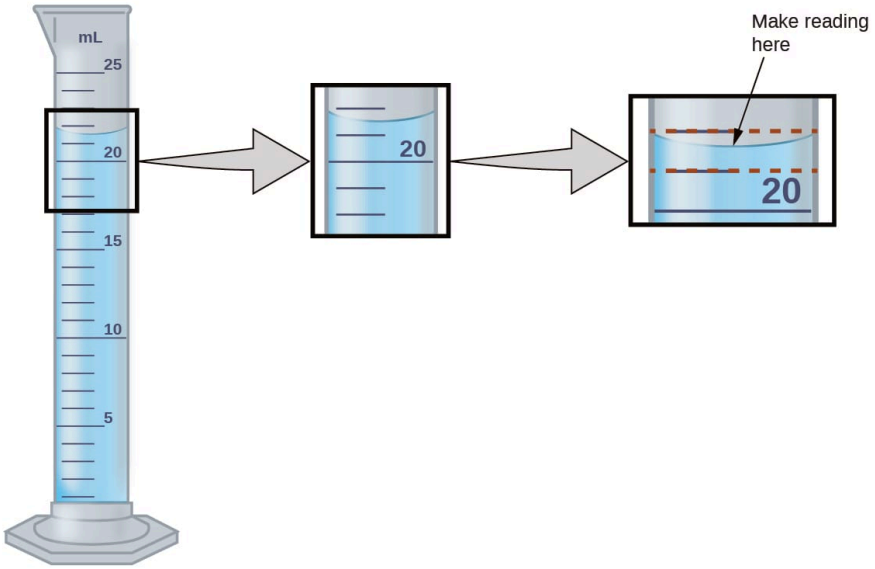


Figure 1.2.2: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a millilitre, and then make a reading (estimate) at the bottom of the meniscus.

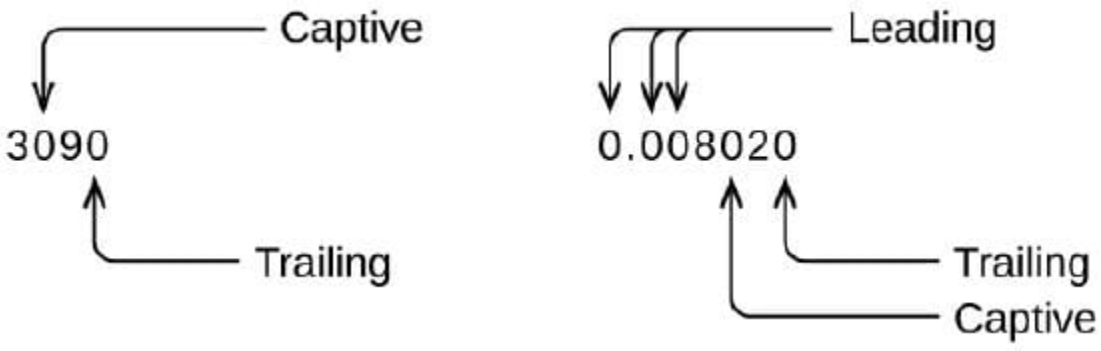
In this case, the meniscus is clearly between 21 and 22 mL and appears closer to 22, so a reasonable estimate would be 21.6 mL. The 2 and 1 are certain, and the 6 is an estimate. Someone else might read 21.5 or 21.7, depending on how they see it. It wouldn't make sense to guess a hundredths place digit as we don't have enough precision.

This same idea applies to digital tools. If an electronic balance displays 6.72 g, the last digit (2) is an estimate—the actual mass is somewhere between 6.71 g and 6.73 g. A more sensitive balance might show 6.723 g, with even greater precision.

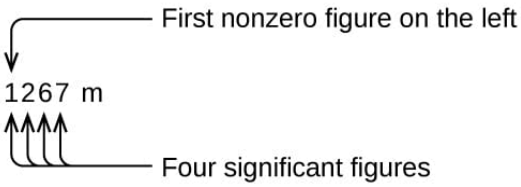
All the digits in a measurement, including the estimated last digit, are called significant figures. They reflect both the measured value and the precision of the tool. When reporting a measurement, the number of significant figures should reflect the precision of the measurement. How do you know which digits are significant?

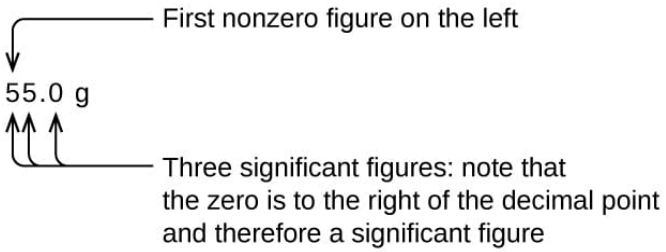
The rules are simple for non-zero digits as they are always significant. Zeros, however, require more attention. We use the terms leading, captive, and trailing to describe different types of zeros:

- Leading zeros come before the first non-zero digit.
- Captive zeros are between non-zero digits.
- Trailing zeros come after the last non-zero digit.

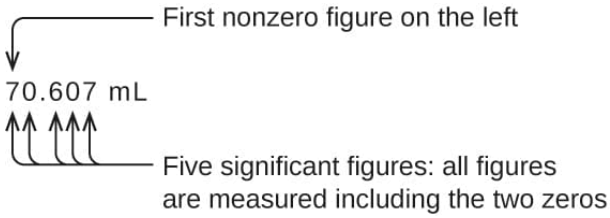


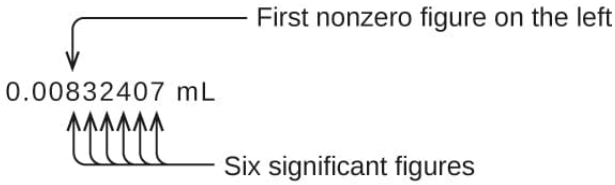
To count significant figures, start with the first non-zero digit on the left and count every digit after that, including zeros (except some trailing zeros that appear before a decimal point). For example:





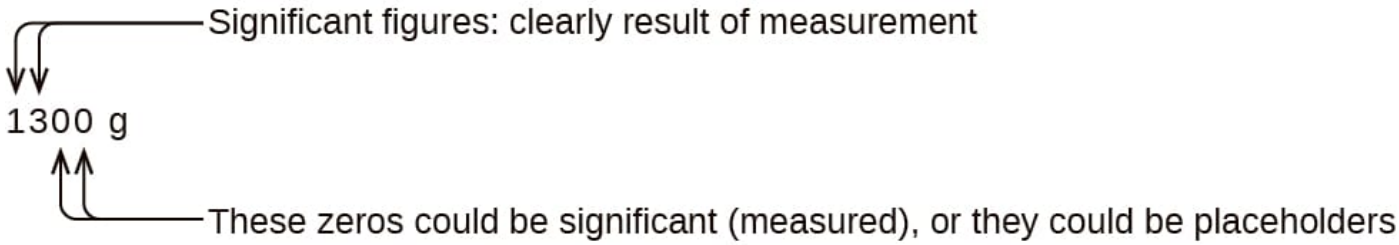
Captive zeros result from measurement and are therefore always significant. Leading zeros (zeros before the first non-zero digit in decimal numbers) are never significant as they merely tell us where the decimal point is located.





To avoid confusion with leading zeros, we often use scientific notation. For example, $0.00832407 = 8.32407 \times 10^{-3}$. This format clearly shows which digits are significant.

What about numbers like 1300 g? The digits 1 and 3 are significant, but it's unclear whether the two zeros were measured or are just placeholders.



To be more precise, we can use scientific notation:

1.3×10^3: 2 significant figures

1.30×10^3: 3 significant figures

1.300×10^3: 4 significant figures

In fact, writing measurements in scientific notation clears up uncertainty about whether zeros are significant or not!

Example 1.2.4

How many significant figures do the following measurements have?

a) 0.00203 g

b) 3.20 cm

c) 1.02 V

Solution

a) 3 significant figures (2, 0, 3; the leading zeros are not significant)

b) 3 significant figures (3, 2, and the trailing 0, which is significant because it comes after the decimal point)

c) 3 significant figures (1, 0, 2; the 0 is a captive zero and always significant)

Exercise 1.2.4

How many significant figures do the following measurements have?

a) 5.070×10^3 L

b) 400 km

c) 1.000 g

Answer available at the end of this section.

In the CHM 135H laboratory, you'll be expected to report measurements using as many digits as can be reliably measured. Including extra digits beyond the precision of your measuring tool doesn't add meaningful information. Since your measurements will often be used in calculations, it's important to know how to keep the correct number of significant figures throughout.

Significant Figures in Calculations

When you do calculations using measurements, your final answer should reflect the least precise value you used. This prevents your answer from appearing more certain than the data allows. While this might seem like an arbitrary set of rules, the significant figures in a final answer are a way of expressing the uncertainty in the data used in the calculation.

To do this, follow these rules:

1. For addition and subtraction:

    Round answers to the same number of decimal places as the value with the *fewest* decimal places.

    Example: 12.11 + 0.3 = 12.41 → 12.4 (1 decimal place)

2. For multiplication and division:

    Round answers to the same number of significant figures as the value with the *fewest* significant figures.

    Example: 3.24 × 7.1 = 23.004 → 23 (2 significant figures)

3. For logarithms (log or ln):

    The number of *decimal places* in the result should equal the number of significant figures in the original number

    Example: log (31) = log (3.1×10^1) = 1.49 (2 significant figures → 2 decimal places)
    This works because the "1" before the decimal comes from the power of 10, while the digits after the decimal reflect the precision of the original number.

    For comparison, consider log(3.1×10^{10}) = 10.49 (2 significant figures → 2 decimal places).

    Notice that in scientific notation, only the exponent changes the part before the decimal point in the logarithm. The precision of the result is always shown in the digits after the decimal place.

4. For antilogarithms (10^x):

The number of significant figures in the result should equal the number of decimal places in the exponent.

Example: $10^{1.49}$ = 31 (2 decimal places → 2 significant figures)

5. For rounding:

If the digit that is dropped is less than 5, round down (leave the last digit unchanged).
If it's 5 or more, round up (increase the last digit by 1).

Note: answers should be rounded only in the final step of the calculation. Each time you round, information is lost; repeated rounding during a calculation leads to accumulated error.

Example 1.2.5: Addition and Subtraction with Significant Figure

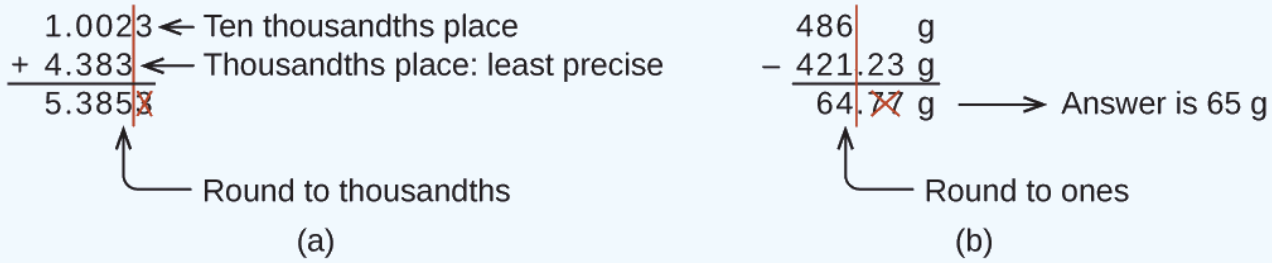
Solve the following and express each answer with the correct number of significant figures.

a) 1.0023 g + 4.383 g =

b) 486 g - 421.23 g =

Solution

Rule: When adding or subtracting, your answer should have the same number of decimal places as the number with the fewest decimal places in the calculation.



Exercise 1.2.5

Solve the following and express each answer with the correct number of significant figures.

a) 2.334 mL + 0.31 mL =

b) 56.533 m - 55.8752 m =

Answer available at the end of this section.

Example 1.2.6: Multiplication and Division with Significant Figures

Solve the following and express each answer with the correct number of significant figures.

a) 0.6238 cm x 6.6 cm =

b) $\frac{421.23\ \text{g}}{486\ \text{mL}} =$

Solution

Rule: When multiplying or dividing numbers, round the result to the same number of digits as the number with the fewest significant figures (the least certain value in terms of multiplication and division).

(a)

$$\underbrace{0.6238\,\text{cm}}_{\text{four significant figures}} \times \underbrace{6.6\,\text{cm}}_{\text{two significant figures}} = 4.11708\,\text{cm}^2 \rightarrow \underbrace{4.1\,\text{cm}^2}_{\text{round to two significant figures}}$$

(b)

$$\underbrace{421.23\,\text{g}}_{\text{five significant figures}} \div \underbrace{486\,\text{mL}}_{\text{three significant figures}} = 0.866728...\,\text{g/mL} \rightarrow \underbrace{0.867\,\text{g/mL}}_{\text{round to three significant figures}}$$

Exercise 1.2.6

Solve the following and express each answer with the correct number of significant figures.

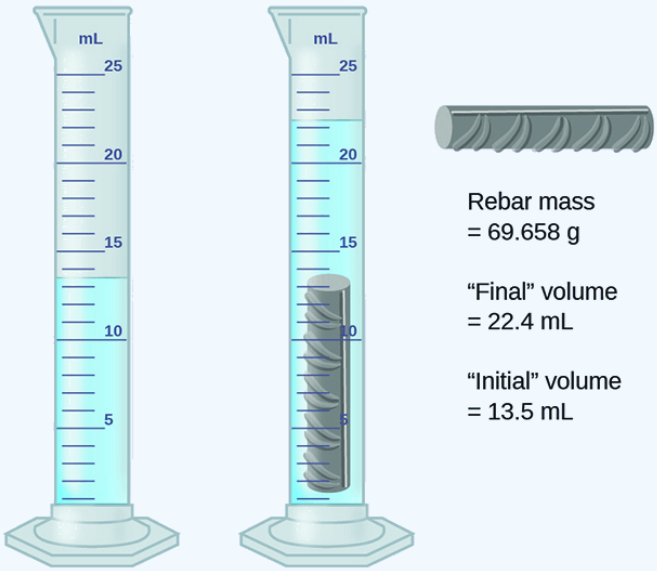
a) 2.334 cm x 0.320 cm =

b) $\frac{55.8753\text{ m}}{56.53\text{ s}} =$

Answer available at the end of this section.

Example 1.2.7: 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.



Use these values to determine the density of this piece of rebar.

Solution

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

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

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

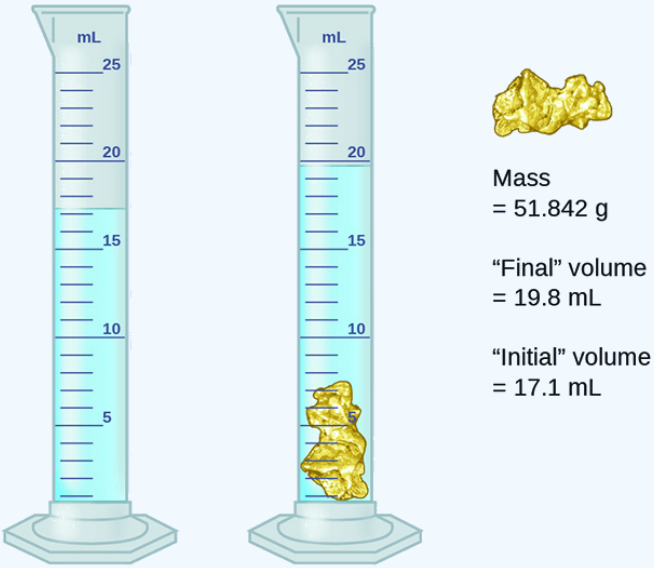
The density is the mass-to-volume ratio:

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

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

Exercise 1.2.7

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



Use these values to determine the density of this material.

Answer available at the end of this section.

Example 1.2.8

Solve the following and express each answer with the correct number of significant figures.

a. $\log(4.5 \times 10^3)$

b. $10^{-2.73}$

Solution

a. The original number has 2 significant figures, so the result is reported with 2 decimal places:

$\log(4.5 \times 10^3) = 3.65$

b. The exponent has 2 decimal places, so the result is reported with 2 significant figures:

$10^{-2.73} = 1.9 \times 10^{-3}$

Exercise 1.2.8

Solve the following and express each answer with the correct number of significant figures.

a. $\log(7.84 \times 10^2)$

b. $10^{3.1}$

Answer available at the end of this section.

Summary

In chemistry, we use the SI (International System of Units) to report measurements in a standardized way. Common base units include the meter (m) for length, kilogram (kg) for mass, and second (s) for time.

Many units used in chemistry are derived from these base units—for example, volume (m^3 or more commonly L) and density (g/cm^3 or g/L).

Unit conversions rely on conversion factors, which are ratios that allow us to express quantities in different units without changing their value.

Significant figures reflect the precision of a measurement, and they must be handled carefully in calculations to avoid overstating certainty. When multiplying or dividing, the result should have the same number of significant figures as the least precise value; when adding or subtracting, the result should be rounded based on decimal places.

Glossary

Celsius (°C)
Unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale.

density
The ratio of mass to volume for a substance or object.

derived SI unit
A unit derived from the seven SI base units.

exact number
Number derived by counting or by definition

kelvin (K)
An SI unit of temperature; 273.15 K = 0 °C.

mass
A fundamental property indicating amount of matter; SI unit is the kilogram (kg).

scientific notation
A convenient method of expressing very large or very small numbers often used by scientists.

SI unit
A standard unit fixed by international agreement in the International System of Units (Le Système International d'Unités)

significant figures
All of the measured digits in a determination, including the uncertain last digit; also called significant digits.

unit conversion factor
Ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit.

volume
: The amount of space occupied by an object.

Answers

Exercise 1.2.1

a)

$$\text{volume } = (0.843 \text{ cm})^3 = 0.599 \text{ cm}^3$$

b.

$$\text{density } = \frac{\text{mass}}{\text{volume}} = \frac{5.34 \text{ g}}{0.599 \text{ cm}^3} = 8.91 \text{ g/cm}^3$$

Exercise 1.2.2

Convert centimetres to millimetres and days to minutes:

$$91 \frac{\cancel{\text{cm}}}{\cancel{\text{day}}} \left(\frac{10 \text{ mm}}{1 \cancel{\text{cm}}} \right) \left(\frac{1 \cancel{\text{day}}}{24 \cancel{\text{h}}} \right) \left(\frac{1 \cancel{\text{h}}}{60 \text{ min}} \right) = 0.63 \text{ mm/min}$$

Exercise 1.2.3

Conversion factors:

1 cm = 10 mm; so 1 cm^3 = (10 mm)^3 = 1000 mm^3

1 mL = 1 cm^3

$$0.038 \cancel{\text{mL}} \left(\frac{1 \cancel{\text{cm}^3}}{1 \cancel{\text{mL}}} \right) \left(\frac{1000 \text{ mm}^3}{1 \cancel{\text{cm}^3}} \right) = 38 \text{ mm}^3$$

Exercise 1.2.4

a) 4 significant figures (5, 0, 7, 0)

b) Ambiguous - could be 1, 2, or 3 significant figures depending on whether the zeros are meant to show precision. Using scientific notation can make this clear.

c) 4 significant figures (1, 0, 0, 0; the trailing zeros after the decimal point are significant)

Exercise 1.2.5

a)

$$\begin{array}{rr} & 2.334 \text{ mL} \\ + & 0.31 \text{ mL} \\ & 2.644 \text{ mL} \end{array}$$

The value with the fewest decimal places (0.31 mL) has 2 decimal places, so the answer should be rounded to 2 decimal places: 2.64 mL

b)

$$\begin{array}{rr} & 56.533 \text{ m} \\ - & 55.8752 \text{ m} \\ & 0.6578 \text{ m} \end{array}$$

The value with the fewest decimal places (56.533 m) has 3 decimal places, so the answer should be rounded to 3 decimal places: 0.658 m.

Exercise 1.2.6

a)

$$\underbrace{2.334 \text{ cm}}_{\text{four significant figures}} \times \underbrace{0.320 \text{ cm}}_{\text{three significant figures}} = 0.74688 \text{ cm}^2 \rightarrow \underbrace{0.747 \text{ cm}^2}_{\text{round to three significant figures}}$$

b)

$$\underbrace{55.8752 \text{ m}}_{\text{six significant figures}} \div \underbrace{56.53 \text{ s}}_{\text{four significant figures}} = 0.988417... \text{ m/s} \rightarrow \underbrace{0.9884 \text{ m/s}}_{\text{round to four significant figures}}$$

Exercise 1.2.7

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

$$\text{volume } = 19.8 \text{ mL} - 17.1 \text{ mL} = 2.7 \text{ mL} = 2.7 \text{ cm}^3$$

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

The density is the mass-to-volume ratio:

$$\text{density } = \frac{\text{mass}}{\text{volume}} = \frac{51.842 \text{ g}}{2.7 \text{ cm}^3} = 19 \text{ g/cm}^3$$

Exercise 1.2.8

a. The original number has 3 significant figures, so the result is reported with 3 decimal places:

$\log(7.84 \times 10^2) = 2.894$

b. The exponent has 1 decimal place, so the result is reported with 1 significant figure:

$10^{3.1} = 1 \times 10^3$

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1.3: Atoms, Elements, and the Mole

Learning Objectives

- Describe the basic structure of an atom, including the location and charge of protons, neutrons, and electrons.
- Define atomic number, mass number, isotope, and ion, and use them to characterize atoms.
- Define a mole and Avogadro's number as a way to count atoms or molecules.
- Convert between mass, moles, and number of atoms using dimensional analysis.

Since chemistry is the study of matter, we need to understand what matter is made of, how we measure it, and how to connect the microscopic and macroscopic worlds. This section introduces the basic building blocks of matter: atoms and elements, how they are organized in the periodic table, and how chemists use the mole to count extremely large numbers of particles. It also introduces molar mass, which links the number of atoms to the mass measured in the lab.

Atoms and Elements

All matter is made of atoms, which are the smallest units of an element that retain its chemical properties. Each atom consists of a dense central nucleus containing positively charged protons and uncharged neutrons, surrounded by negatively charged electrons. The nucleus contains nearly all of the atom's mass, while the electrons occupy most of its 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. To appreciate just how small the nucleus is compared to the whole atom, if the nucleus were the size of a blueberry, the atom would be the size of a football stadium.(Figure 1.3.1).

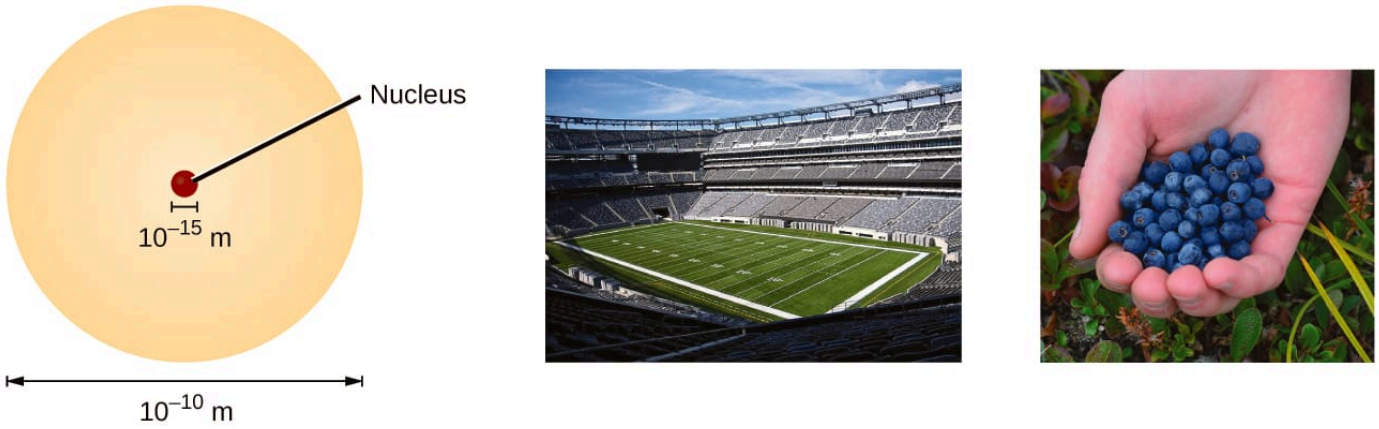


Figure 1.3.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Each element is defined by its number of protons, called the atomic number (Z). For example, all carbon atoms have 6 protons. Atoms of the same element can have different numbers of neutrons, and these are called isotopes. The mass number (A) of an atom is the total number of protons and neutrons.

Atomic number (Z) = number of protons

Mass number (A) = number of protons + neutrons

Number of neutrons = $A - Z$

Atoms are electrically neutral when they have the same number of electrons as protons. If an atom gains or loses electrons, it becomes an ion, a charged particle.

- Cation: more protons than electrons (positive charge)

- Anion: more electrons than protons (negative charge)

Chemical Symbols, Isotopes, and Atomic Mass

Each element is represented by a one- or two-letter chemical symbol. For example, the symbol for hydrogen is H, carbon is C, and sodium is Na (from the Latin *natrium*). These symbols are used to represent both individual atoms and large amounts of an element. For example, Fe can mean a single iron atom or a sample of iron metal, depending on the context. Only the first letter is capitalized: Co is cobalt, while CO is the compound carbon monoxide.

Some common elements and their symbols are shown below:

Element	Symbol	Element	Symbol
Hydrogen	H	Oxygen	O
Carbon	C	Nitrogen	N
Sodium	Na	Chlorine	Cl
Iron	Fe	Calcium	Ca
Copper	Cu	Silver	Ag
Gold	Au	Lead	Pb

Atoms of the same element can have different numbers of neutrons. These are called isotopes. For example, all carbon atoms have 6 protons, but they can have 6, 7, or 8 neutrons corresponding to carbon-12, carbon-13, and carbon-14, respectively. Isotopes are written using the element symbol with the mass number (protons + neutrons) as a superscript:

$^{12}\mathrm{C}, {}^{13}\mathrm{C}, {}^{14}\mathrm{C}$

The atomic mass listed on the periodic table is a weighted average of the masses of all naturally occurring isotopes of that element. For example, boron has two isotopes:

- $^{10}\mathrm{B}$, about 20%, mass = 10.0129 amu
- $^{11}\mathrm{B}$, about 80%, mass = 11.0093 amu

The average atomic mass of boron is:

$$(0.20 \times 10.0129) + (0.80 \times 11.0093) = 10.81 \text{ amu}$$

This is why atomic masses on the periodic table are often decimals, not whole numbers.

The atomic mass unit (amu) is defined as exactly one-twelfth the mass of a carbon-12 atom:
1 amu = 1/12 the mass of a $^{12}\mathrm{C}$ atom = 1.6605×10^{-24} g

Protons and neutrons each have masses close to 1 amu, while electrons are much lighter.

Green Chemistry Connection: Endangered Elements

Helium naturally forms from the radioactive decay of uranium and thorium and can found in natural gas deposits from which it can be extracted. Helium's extremely low boiling point of -269 °C or 4 K makes it vital for applications requiring cooling to temperatures close to absolute zero. These applications include magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR) spectroscopy that rely on super conducting magnets. This makes helium essential for scientific discovery and human wellbeing as it supports health diagnoses and treatment. This makes the sustainable use of helium an important target for the United Nations sustainability development goals #3 Good Health and Wellbeing (see appendix for more information). However, once helium becomes released into the atmosphere it can escape earth's gravitational pull and be lost to space, making it the only truly unrecoverable element.

In 2018, it was estimated that as much as 15% of the global helium consumption was used for entertainment (e.g. party balloons). So, before buying balloons for your next party, consider that helium will likely be lost forever and thus is taken away from critical medicine and science applications.



Figure 1.3.2: From left to right: 1) UN Sustainable Development Goal #3 (image by United Nations, Public domain, via Wikimedia Commons) 2) Medical MRI scanner (image by Jan Ainali, CC BY 3.0 <https://creativecommons.org/licenses/by/3.0>, via Wikimedia CommonsPaste), 3) Nuclear Magnetic Resonance (NMR) Spectrometer (image by SamihaAlam1999, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons)

Periodic Table

As chemists discovered more elements, they noticed that some had similar properties and could be grouped together. For example, lithium (Li), sodium (Na), and potassium (K) all react strongly, form similar compounds, and are shiny metals. Calcium (Ca), strontium (Sr), and barium (Ba) also share properties but behave differently than Li, Na, and K. Other elements, like fluorine (K), chlorine (Cl), bromine (Br), and iodine (I), also form a group with similar behaviors.

In 1869, Dmitri Mendeleev arranged the known elements into a table based on their properties and increasing atomic mass. He even left gaps for elements that hadn't been discovered yet and predicted their properties. When these elements (like gallium and germanium) were later found, it confirmed his idea.

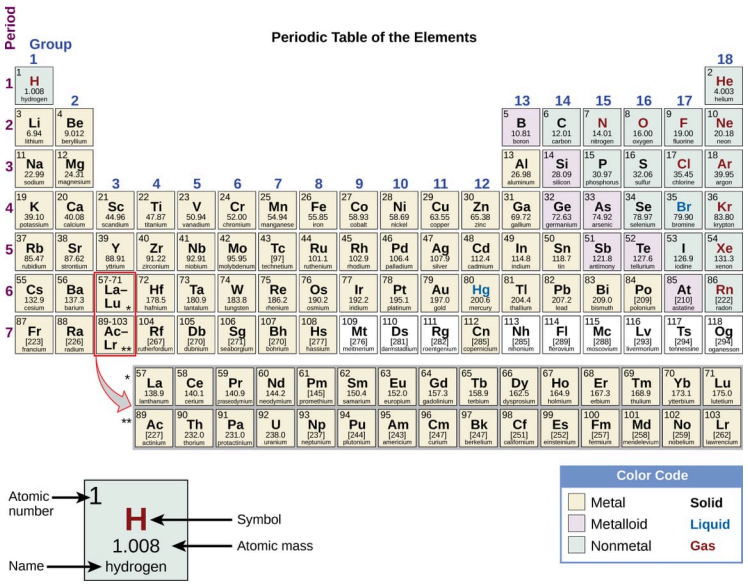


Figure 1.3.3: Elements in the periodic table are organized according to their properties.

Today's periodic table is organized by increasing atomic number (number of protons), not atomic mass. Elements with similar chemical properties are placed in vertical columns called groups, and horizontal rows are called periods. There are 18 groups and 7 periods.

Elements are broadly classified into:

- Metals: shiny, good conductors, malleable and ductile (yellow on Figure 1.3.3)
- Nonmetals: dull, poor conductors (green on Figure 1.3.3)
- Metalloids: have properties between metals and nonmetals (pink on Figure 1.3.3)

Figure 1.3.4 shows more specific classifications. The main group elements are groups 1, 2, and 13–18, while the transition metals are groups 3–12 and the lanthanides and actinides are shown below the table. Groups also have names, such as alkali metals for Group 1, alkaline earth metals for Group 2, halogens for Group 17 and noble gases for Group 18.

Hydrogen is unique for reasons we will see in Chapter 2. It's placed above group 1 but has some properties like group 17.

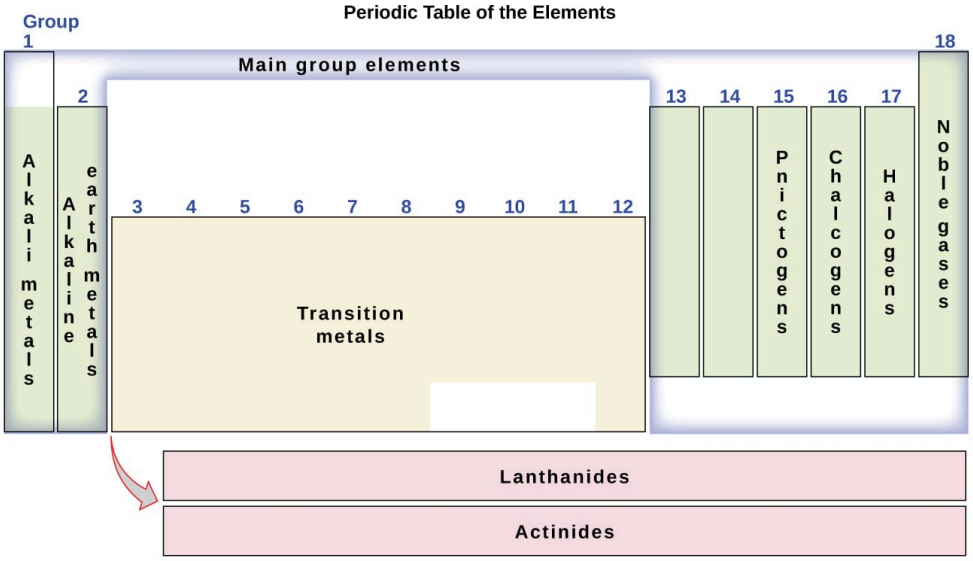


Figure 1.3.4: The periodic table organizes elements with similar properties into groups.

The periodic table helps scientists understand and predict how elements behave. For example, chemist Gertrude

Elion (1918-1999) used similarities between sulfur and oxygen (both in Group 16) to design drugs that interfered with DNA replication. Her work led to treatments for leukemia and earned her a Nobel Prize in 1988.

You will use the periodic table frequently throughout CHM 135H to understand atomic structure, chemical bonding, and periodic trends.

Chemistry in Everyday Life: Chemistry of Cell Phones

It's hard to imagine modern life without cell phones (Figure 1.3.5). These devices rely on a wide range of chemical elements, including rare earth metals and transition metals, which are essential for their advanced functionality. In fact, nearly one-third of all naturally occurring elements are used in a typical smartphone. Each element plays a role in the phone's design, structure, and function.

The case is made from strong plastics (polymers containing carbon, hydrogen, oxygen, and nitrogen) and lightweight metals such as aluminum and magnesium. The screen is made from toughened glass containing silicon, aluminum, sodium, and potassium, and coated with a transparent conductor like indium tin oxide. Inside, the circuit board includes silicon, copper, tin, silver, and gold, along with less familiar elements like yttrium and gadolinium. The battery uses lithium ions and other materials such as cobalt, iron, and copper.



Figure 1.3.5: Almost one-third of naturally occurring elements are used to make a cell phone. (credit: modification of work by John Taylor)

Moles and Avogadro's Number

Atoms and molecules are far too small to count individually in the lab. For example, one atom of carbon weighs less than 2×10^{-23} grams. To work with chemical amounts more easily, chemists use a counting unit called the mole.

A mole is defined as exactly 6.022×10^{23} particles. This number is called Avogadro's number, and it is similar in concept to a dozen (12), except that it is much larger. One mole of atoms contains 6.022×10^{23} atoms; one mole of molecules contains 6.022×10^{23} molecules.

Because the mass of a single atom is so small, the mole also provides a useful connection between atomic masses (in amu) and masses in grams. The mass of one mole of atoms in grams is equal to the atomic mass of the element in amu. For example:

- One atom of carbon-12 has a mass of 12.00 amu.
- One mole of carbon-12 atoms has a mass of 12.00 g.

This means we can use the mole to convert between the number of atoms or molecules and the mass of a sample, a skill that will be used often throughout this course.

Example 1.3.1

Use the relationships between moles, number of atoms, and molar mass to answer the following:

a. How many atoms are present in 1.00 mole of Cu atoms?
b. What is the mass of 1.00 mole of Cu?
c. How many atoms are present in 2.50 moles of Cu?
d. What is the mass of 2.50 moles of Cu?

Solution

The number of atoms in one mole is given by Avogadro's number, $6.022 \times 10^{23}\ \mathrm{atoms/mol}$.
The molar mass of copper (Cu) is 63.55 g/mol.

a) $1.00\ \mathrm{mol\ Cu} \times \frac{6.022 \times 10^{23}\ \mathrm{atoms}}{1\ \mathrm{mol}} = 6.022 \times 10^{23}\ \mathrm{atoms}$

b) $1.00\ \mathrm{mol\ Cu} \times \frac{63.55\ \mathrm{g}}{1\ \mathrm{mol}} = 63.55\ \mathrm{g}$

c) $2.50\ \mathrm{mol\ Cu} \times \frac{6.022 \times 10^{23}\ \mathrm{atoms}}{1\ \mathrm{mol}} = 1.506 \times 10^{24}\ \mathrm{atoms}$

d) $2.50\ \mathrm{mol\ Cu} \times \frac{63.55\ \mathrm{g}}{1\ \mathrm{mol}} = 158.9\ \mathrm{g}$

Exercise 1.3.1

a) How many atoms are present in 0.35 mole of N atoms?

b) What is the mass of 0.35 moles of N?

Answer available at the end of this section.

Example 1.3.2

How many atoms of aluminium (Al) are present in a 12.23 g sample?

Solution

To find the number of atoms, we convert grams to moles using the molar mass of Al, then convert moles to atoms using Avogadro's number.

Molar mass of Al = 26.98 g/mol
Avogadro's number = $6.022 \times 10^{23}\ \mathrm{atoms/mol}$

Step 1: Convert grams to moles:
$12.23\ \mathrm{g\ Al} \times \frac{1\ \mathrm{mol}}{26.98\ \mathrm{g}} = 0.4533\ \mathrm{mol\ Al}$

Step 2: Convert moles to atoms:
$0.4533\ \mathrm{mol\ Al} \times \frac{6.022 \times 10^{23}\ \mathrm{atoms}}{1\ \mathrm{mol}} = 2.730 \times 10^{23}\ \mathrm{atoms}$

Alternatively, this can be done as a single combined step:

$12.23\ \mathrm{g\ Al} \times \frac{1\ \mathrm{mol}}{26.98\ \mathrm{g}} \times \frac{6.022 \times 10^{23}\ \mathrm{atoms}}{1\ \mathrm{mol}} = 2.730 \times 10^{23}\ \mathrm{atoms}$

Exercise 1.3.2

What is the mass of 1.08×10^{22} gold (Au) atoms?

Answer available at the end of this section.

Summary

All matter is made of atoms, which consist of a nucleus (protons and neutrons) and surrounding electrons. Atoms of the same element have the same number of protons (atomic number), but may have different numbers of neutrons (isotopes).

Elements are represented by chemical symbols and organized in the periodic table by atomic number. Elements in the same group share chemical properties.

Atomic mass is a weighted average of an element's naturally occurring isotopes and is reported in atomic mass units (amu).

The mole is a counting unit used to relate the number of atoms to measurable quantities. One mole contains 6.022×10^{23} particles (Avogadro's number).

The molar mass of an element (in g/mol) is numerically equal to its atomic mass (in amu). It links the microscopic scale (atoms) to the macroscopic scale (grams).

You can convert between mass, moles, and number of atoms using dimensional analysis:

- Atoms ↔ Moles: Use Avogadro's number.
- Moles ↔ Mass: Use molar mass.

Glossary

actinide
: An element of the set of transition metals located below the main table, with lanthanides.

alkali metal
: Element in group 1.

alkaline earth metal
: Element in group 2.

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

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

atomic mass
: The average mass of atoms of an element, expressed in atomic mass units (amu).

atomic mass unit (amu)
: The unit of mass equal to 1/12 of the mass of a ^{12}C atom; also called unified atomic mass unit (u) or Dalton (Da).

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

Avogadro's number (N_A)
: The experimentally-determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} mol^{-1}.

cation
A positively-charged atom or molecule (contains fewer electrons than protons).

chalcogen
Element in group 16.

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

electron
A negatively-charged subatomic particle of relatively low mass located outside the nucleus.

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

group
Vertical column of the periodic table.

halogen
Element in group 17.

ion
An electrically-charged atom or molecule (contains unequal numbers of protons and electrons).

isotope
An atom that contains the same number of protons but different number of neutrons.

lanthanide
An element of the set of transition metals located below the main table, with actinides.

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

matter
Anything that occupies space and has mass.

metal
An element that is shiny, malleable, and good conductor of heat and electricity.

metalloid
An element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors.

molar mass
The mass in grams of 1 mole of a substance.

mole
The amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C.

molecule
A bonded collection of two or more atoms of the same or different elements.

neutron
An uncharged, subatomic particle located in the nucleus.

noble gas
Element in group 18; also called inert gas.

nonmetal
An element that appears dull, a poor conductor of heat and electricity.

nucleus
: The massive, positively charged center of an atom made up of protons and neutrons.

period
: Horizontal row of the periodic table; also called a series.

pnictogen
: Element of group 15.

proton
: A positively charged, subatomic particle located in the nucleus.

transition metal
: Element in groups 3-11.

Answers

Exercise 1.3.1

a) $0.35\ \text{mol N} \times \frac{6.022 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} = 2.11 \times 10^{23}\ \text{atoms}$

b) The molar mass of nitrogen atoms (N) is 14.01 g/mol.

$0.35\ \text{mol N} \times \frac{14.01\ \text{g}}{1\ \text{mol}} = 4.9\ \text{g}$

Exercise 1.3.2

To find the mass, we first convert atoms to moles using Avogadro's number, then convert moles to grams using the molar mass of gold.

Molar mass of Au = 196.97 g/mol

Avogadro's number = $6.022 \times 10^{23}\ \text{atoms/mol}$

Step 1: Convert atoms to moles:

$1.08 \times 10^{22}\ \text{atoms Au} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} = 0.01793\ \text{mol Au}$

Step 2: Convert moles to grams:

$0.01793\ \text{mol Au} \times \frac{196.97\ \text{g}}{1\ \text{mol}} = 3.53\ \text{g}$

Or in a single step:

$1.08 \times 10^{22}\ \text{atoms Au} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} \times \frac{196.97\ \text{g}}{1\ \text{mol}} = 3.53\ \text{g}$

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1.4: Compounds and How We Represent Them

Learning Objectives

- Distinguish between ionic and covalent compounds.
- Interpret chemical formulas to determine the types, ratios, and charges of ions or atoms in a compound.
- Recognize the difference between molecular formulas, empirical formulas, and formula units.
- Identify simple ionic and covalent compounds by name or formula, including those with common polyatomic ions.

Atoms are the building blocks of matter, but they are rarely found alone. In nature, atoms usually join with other atoms to form compounds. These combinations happen because atoms in chemical bonds are often more stable than the same atoms on their own. This section will cover how atoms form salts through ionic bonding and molecules through covalent bonding, how to write and interpret chemical formulas, and how to name simple compounds. These ideas are essential for understanding chemical reactions, which happen when atoms and compounds rearrange to form new substances.

Types of Chemical Bonds

What causes atoms to form bonds with other atoms, rather than remain separate? The short answer is that bonding lowers the energy of a system, making compounds more stable than isolated atoms.

There are three idealized types of bonding, based on how electrons interact between atoms. In this section, we will focus primarily on ionic and covalent bonding.

1. Ionic bonding occurs when positively and negatively charged ions are held together by electrostatic forces. This type of bonding commonly occurs between metals and nonmetals. To produce the ions involved in the ionic bond, their neutral atoms would have to gain electrons (to form negative ions called anions) or lose electrons (to form positive ions called cations), though this process may happen in a separate reaction. For example, sodium (Na) and chlorine (Cl) form sodium chloride, NaCl.
    - Ionic compounds do not form molecules. Instead, the ions are arranged in a large, repeating lattice. The chemical formula NaCl represents the simplest ratio of ions (1:1) and is called a *formula unit*, not a molecule.
2. Covalent bonding occurs when atoms share electrons in a molecule or a polyatomic ion. This type of bonding occurs most often between nonmetals. For example, hydrogen (H) and oxygen (O) form water, $\mathrm{H_2O}$.
    - Covalent compounds consist of individual molecules. The formula $\mathrm{H_2O}$ tells you which atoms are in each molecule: 2 hydrogen atoms and 1 oxygen atom.
3. Metallic bonding occurs when valence electrons are delocalized across many atoms in a metal, forming a "sea of electrons" that allows metals to conduct electricity and be malleable.

Although we describe these as three distinct types, bonding exists on a continuum. Some bonds have both ionic and covalent character, depending on how much electron sharing or transfer occurs. Bonding will be covered in more detail in Chapter 3. For now, focus on recognizing whether a compound is ionic or covalent and whether its formula represents a molecule or a formula unit.

Ions and Charge in Ionic Compounds

When atoms gain or lose electrons, they form charged particles called ions. Metals tend to lose electrons to form positive ions (cations), while nonmetals tend to gain electrons to form negative ions (anions). These ions are held together in ionic compounds by electrostatic attraction.

The periodic table can help predict the charges of many common ions. For main-group elements, there is a useful pattern:

Group 1 elements form 1+ ions (e.g. $\mathrm{Na^+}$)

Group 2 elements form 2+ ions (e.g. $\mathrm{Ca^{2+}}$)

Group 17 (halogens) form 1– ions (e.g. $\mathrm{Cl^-}$)

Group 16 elements form 2– ions (e.g. $\mathrm{O^{2-}}$)

These trends work well for many main-group elements. Transition metals (in the middle of the table), however, often form ions with more than one possible charge. For example, iron can form $\mathrm{Fe^{2+}}$ or $\mathrm{Fe^{3+}}$, and copper can form $\mathrm{Cu^+}$ or $\mathrm{Cu^{2+}}$.

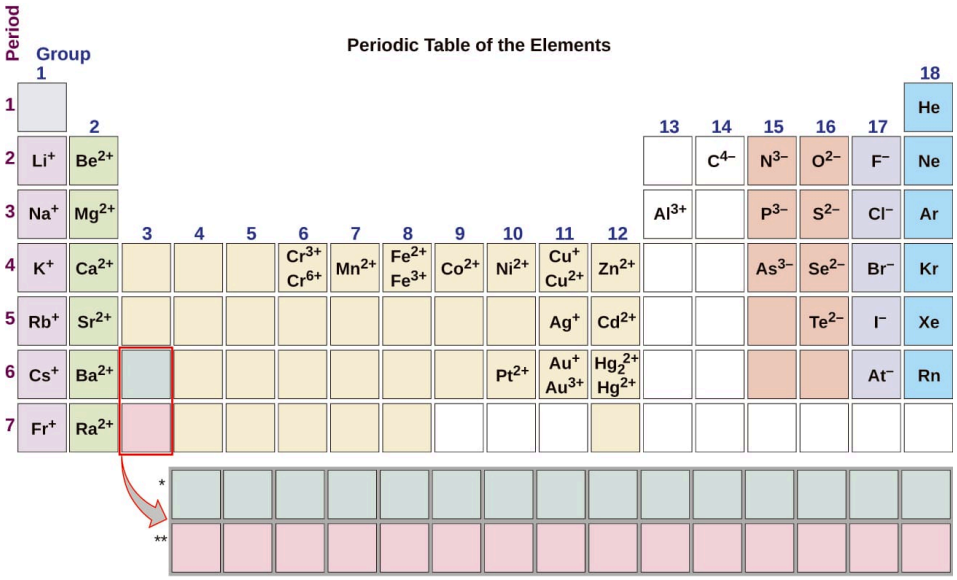


Figure 1.4.1: Some elements exhibit a regular pattern of ionic charge when they form ions.

All ionic compounds are electrically neutral overall. That means the total positive charge from the cations must equal the total negative charge from the anions. The chemical formula reflects this balance.

For example:

- In NaCl, one $\mathrm{Na^+}$ balances one $\mathrm{Cl^-}$.
- In $\mathrm{CaCl_2}$, one $\mathrm{Ca^{2+}}$ balances two $\mathrm{Cl^-}$.

Example 1.4.1: Formation of Ions

Magnesium and nitrogen react to form an ionic compound.

- Predict which element forms the cation and which forms the anion.
- Determine the charge on each ion, and write its symbol and name.
- Explain how the charges balance in the compound.

Solution

Magnesium is a metal in group 2. Metals form positive ions (cations). A magnesium atom loses two electrons to form a $\mathrm{Mg^{2+}}$ ion.

Nitrogen is a nonmetal in group 15. Nonmetals form negative ions (anions). A nitrogen atom gains three electrons to form a $\mathrm{N^{3-}}$ ion.

To form a neutral compound, the total positive and negative charges must be equal:

- Each $\mathrm{Mg^{2+}}$ has a charge of +2.
- Each $\mathrm{N^{3-}}$ has a charge of –3.

The lowest whole-number ratio that balances the charges is 3 $\mathrm{Mg^{2+}}$ and 2 $\mathrm{N^{3-}}$:

$(3 \times +2) + (2 \times -3) = +6 - 6 = 0$

So the formula of the neutral compound is $\mathrm{Mg_3N_2}$.

Exercise 1.4.1

Aluminum and oxygen react to form an ionic compound.

- Which element forms the cation? Which forms the anion?
- What is the charge on each ion? Write the symbol and name for each.
- How do the charges balance? What is the formula of the compound?

Answer available at the end of this section.

Representing Compounds

Chemists use different types of formulas and models to represent compounds, as shown in Figure 1.4.2 for methane:

- A chemical formula shows the types and numbers of atoms in a substance.
- A structural formula shows how the atoms are connected.
- A ball-and-stick model uses spheres for atoms and sticks for bonds to show the 3D shape of the molecule.
- A space-filling model shows the relative sizes of atoms and how they fill space in a molecule.

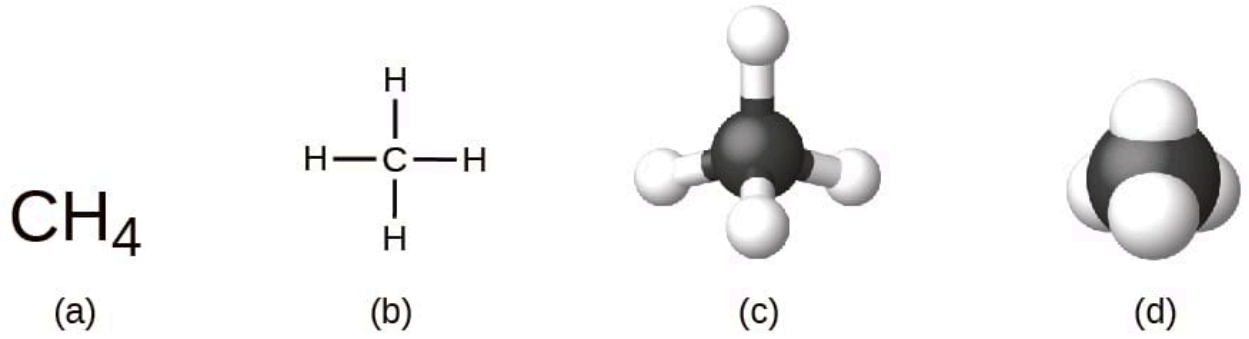


Figure 1.4.2 : A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

It's important to understand the difference between subscripts and coefficients (Figure 1.4.3):

- $\mathrm{H_2}$ means a molecule made of two bonded hydrogen atoms
- 2 H means two separate hydrogen atoms, not bonded
- 2 $\mathrm{H_2}$ means two molecules of diatomic hydrogen

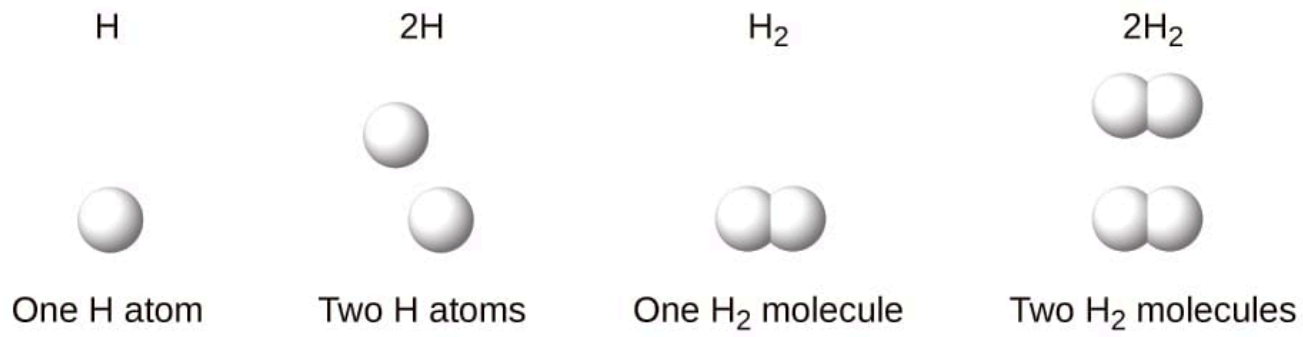


Figure 1.4.3 : The symbols H, $2\,\mathrm{H}$, $\mathrm{H_2}$, and $2\,\mathrm{H_2}$ represent very different entities.

Subscripts tell you how many atoms of each element are in a molecule or formula unit. For example, $\mathrm{C_2H_6O}$ contains 2 carbon, 6 hydrogen, and 1 oxygen atom. Coefficients in front of a formula show how many copies of that substance are present, whether counting in atoms, molecules, or moles.

These numbers help you calculate amounts of atoms, molecules, or moles. For example:

- One molecule of $\mathrm{C_2H_6O}$ contains 6 hydrogen atoms.
- One mole of $\mathrm{C_2H_6O}$ contains 6 moles of hydrogen atoms.

In the next section, you will see how these ideas are used to interpret chemical equations and perform stoichiometric calculations.

Empirical and Molecular Formulas

A chemical formula shows the types of atoms in a compound and how many of each atom are present. There are two main kinds of formulas:

- A molecular formula shows the actual number of atoms of each element in a molecule.
  - Example: The molecular formula for acetic acid (found in vinegar) is $\mathrm{C_2H_4O_2}$. This means each molecule has 2 carbon atoms, 4 hydrogen atoms, and 2 oxygen atoms.
- An empirical formula shows the simplest whole-number ratio of atoms in a compound.
  - Example: The empirical formula for acetic acid is $\mathrm{CH_2O}$. The 2:4:2 ratio simplifies to 1:2:1.

The molecular formula is always a whole-number multiple of the empirical formula. Sometimes, the empirical and molecular formulas are the same. For example, $\mathrm{H_2O}$ is both the empirical and molecular formula for water.

Knowing the molecular formula tells you how many atoms are in a molecule, but not how they are connected. Different compounds can have the same molecular formula but different structures. These are called isomers, and they often have very different properties.

Molar Mass

The molar mass of a compound is the mass of one mole of its particles, expressed in grams per mole (g/mol). To calculate it, add up the atomic masses of all the atoms in the chemical formula.

For example, the molar mass of water ($\mathrm{H_2O}$) is: 2(1.01 g/mol for H) + (16.00 g/mol for O) = 18.02 g/mol

This tells us that 1 mole of water molecules has a mass of 18.02 grams.

You'll use molar mass to convert between the number of particles, the number of moles, and the mass of a substance.

Example 1.4.2

An average cup of coffee has 130 mg of caffeine, $C_8H_{10}N_4O_2$. How many moles of caffeine are in a cup of coffee? How many caffeine molecules?

Solution

Step 1: Calculate the molar mass of caffeine.

Caffeine has the formula $C_8H_{10}N_4O_2$. We find the molar mass by adding up the masses of all the atoms:

- Carbon: $8 \times 12.01 = 96.08\ \text{g/mol}$
- Hydrogen: $10 \times 1.008 = 10.08\ \text{g/mol}$
- Nitrogen: $4 \times 14.01 = 56.04\ \text{g/mol}$
- Oxygen: $2 \times 16.00 = 32.00\ \text{g/mol}$

Total molar mass = $96.08 + 10.08 + 56.04 + 32.00 = 194.20\ \text{g/mol}$

Step 2: Convert mass to moles.

We are given 130 mg of caffeine, which we first convert to grams:

$$130\ \text{mg} \times \frac{1\ \text{g}}{1000\ \text{mg}} = 0.130\ \text{g}$$

Now, use the molar mass to find the moles of caffeine:

$$0.130\ \text{g} \times \frac{1\ \text{mol}}{194.20\ \text{g}} = 0.000669\ \text{mol}$$

Step 3: Calculate the number of molecules.

Use Avogadro's number, $6.022 \times 10^{23}\ \text{molecules/mol}$, to find the number of molecules:

$$0.000669\ \text{mol} \times 6.022 \times 10^{23}\ \frac{\text{molecules}}{\text{mol}} = 4.03 \times 10^{20}\ \text{molecules}$$

Exercise 1.4.2

A student dissolves 2.50 g of table salt, $NaCl$, in water to make a saline solution.

a) How many moles of $NaCl$ are in the solution?
b) How many formula units of $NaCl$ are in the solution?

Answer available at the end of this section.

Naming Compounds

Chemists use specific rules to name compounds. You don't need to memorize all the rules, but it helps to recognize some common patterns.

1. Ionic Compounds

- Made of a metal and a nonmetal
- Name the metal first, then the nonmetal with "-ide"
  - $NaCl$: sodium chloride
  - MgO: magnesium oxide

- Some metals can form more than one ion. We show the charge with Roman numerals:
  - $\mathrm{FeCl_2}$: iron(II) chloride
  - $\mathrm{FeCl_3}$: iron(III) chloride

2. Covalent Compounds

- Made of two nonmetals
- Use prefixes to show how many atoms of each element
  - $\mathrm{CO_2}$: carbon dioxide
  - $\mathrm{N_2O_4}$: dinitrogen tetroxide
- The first element does not get a prefix if there's only one atom
  - CO: carbon monoxide (not *monocarbon monoxide*)

3. Polyatomic Ions

Some ionic compounds contain polyatomic ions, a group of two or more atoms that are covalently bonded together and carry a charge:

- $\mathrm{NaNO_3}$: sodium nitrate
- $\mathrm{CaSO_4}$: calcium sulfate
- $\mathrm{NH_4Cl}$: ammonium chloride

A few polyatomic ions are worth recognizing:

Name	Formula
Ammonium	$\mathrm{NH_4^+}$
Nitrate	$\mathrm{NO_3^-}$
Sulfate	$\mathrm{SO_4^{2-}}$
Carbonate	$\mathrm{CO_3^{2-}}$
Hydroxide	$\mathrm{OH^-}$
Phosphate	$\mathrm{PO_4^{3-}}$

Summary

Most elements are found in nature as part of compounds. Compounds form when atoms are held together by chemical bonds. In ionic compounds, oppositely charged ions are held together by electrostatic attraction. In covalent compounds, atoms are held together by shared electrons.

Ionic compounds are made of formula units arranged in a crystal lattice. Covalent compounds are made of individual molecules.

Chemical formulas and names show which elements are present and in what ratios. Subscripts show how many atoms of each element are in a unit, and coefficients show how many units there are. These ideas are the foundation for understanding chemical reactions.

The molar mass of a compound allows us to convert between the mass and the number of moles.

Glossary

ball-and-stick model
: 3D representation of molecules using spheres for atoms and sticks for bonds.

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

covalent bonding
: Occurs when electrons are shared between atoms in a molecule or a polyatomic ion; most often occurs between nonmetals.

electrostatic attraction
: Attraction between an atom's positively charged nucleus and the negatively charged electrons of another atom; responsible for ionic bonding.

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

formula unit
: The simplest ratio of ions in an ionic compound.

ionic bonding
: Occurs when a metal donates one or more electrons to a nonmetal, forming oppositely charged ions.

metallic bonding
: Occurs when valence electrons are delocalized across many atoms in a metal, forming a "sea of electrons" that allows metals to conduct electricity and be malleable.

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.

polyatomic ion
: An ion composed of more than one atom.

space-filling model
: 3D representation of molecules using spheres to show the relative size of atoms and how they fill space.

structural formula
: Formula that shows the atoms in a molecule and how they are connected.

Answers

Exercise 1.4.1

Aluminum is a metal in group 13. Metals form positive ions (cations). An aluminum atom loses three electrons to form a $\mathrm{Al^{3+}}$ ion.

Oxygen is a nonmetal in group 16. Nonmetals form negative ions (anions). An oxygen atom gains two electrons to form a $\mathrm{O^{2-}}$ ion.

To form a neutral compound, the total positive and negative charges must be equal:

- Each $\mathrm{Al^{3+}}$ has a charge of +3.
- Each $\mathrm{O^{2-}}$ has a charge of –2.

The lowest whole-number ratio that balances the charges is 2 $\mathrm{Al^{3+}}$ and 3 $\mathrm{O^{2-}}$:

$(2 \times +3) + (3 \times -2) = +6 - 6 = 0$

So the formula of the neutral compound is $\mathrm{Al_2O_3}$.

Exercise 1.4.2

Step 1: Calculate the molar mass of NaCl.

Sodium (Na): 22.99 g/mol

Chlorine (Cl): 35.45 g/mol

Total molar mass = $22.99 + 35.45 = 58.44\ \mathrm{g/mol}$

Step 2: Calculate moles of NaCl.

Use:

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$2.50\ \mathrm{g} \times \frac{1\ \mathrm{mol}}{58.44\ \mathrm{g}} = 0.0428\ \mathrm{mol}$$

Step 3: Calculate the number of formula units.

Use Avogadro's number, $6.022 \times 10^{23}\ \text{formula units/mol}$:

$$0.0428\ \mathrm{mol} \times 6.022 \times 10^{23}\ \frac{\text{formula units}}{\mathrm{mol}} = 2.58 \times 10^{22}\ \text{formula units}$$

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1.5: Chemical Reactions and Equations

Learning Objectives

- Interpret a chemical equation to identify the reactants, products, and their relative quantities.
- Balance a chemical equation to reflect the conservation of atoms during a chemical reaction.

Chemical reactions are at the heart of chemistry. They drive everything from the discovery of new medicines to the development of cleaner fuels and advanced materials. In a chemical reaction, atoms are rearranged to form new substances with new properties. Chemists use chemical equations to represent these changes in a clear, symbolic way.

A chemical equation shows what substances react (called reactants) and what substances are produced (called products). The formulas of the substances appear on either side of a reaction arrow, and coefficients in front of each formula tell us how many particles (or moles) are involved.

For example, the combustion of methane is shown in Figure $1.5.1$. One methane molecule ($\mathrm{CH_4}$) reacts with two oxygen molecules ($\mathrm{O_2}$) to form one carbon dioxide molecule ($\mathrm{CO_2}$) and two water molecules ($\mathrm{H_2O}$).

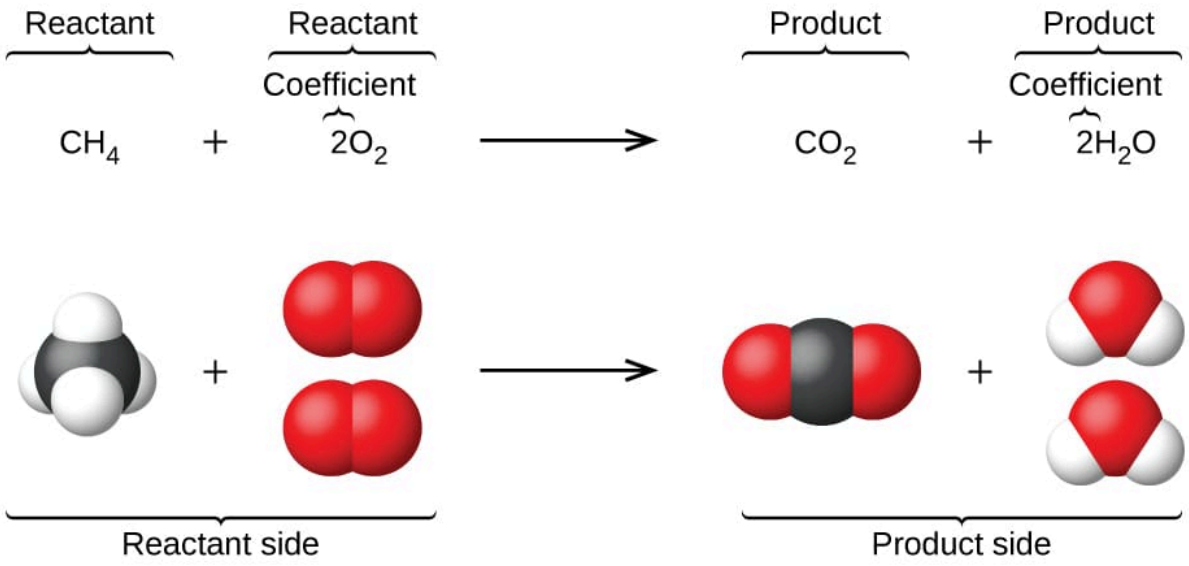


Figure $1.5.1$: The reaction between methane and oxygen to produce carbon dioxide and water. The top shows the balanced chemical equation using formulas. The bottom shows space-filling models for each molecule.

This example shows the key parts of any chemical equation:

1. Reactants are listed on the left side of the arrow
2. Products are listed on the right side of the arrow.
3. Plus signs (+) separate different substances.
4. An arrow separates the reactant and product (left and right) sides of the equation.
5. Coefficients in front of formulas show how many units (atoms, molecules, or moles) are involved.

The chemical equation represents how many of each type of particle is involved, not just what changes. A balanced chemical equation also reflects the law of conservation of mass: atoms are neither created nor destroyed in a chemical reaction, rather rearranged.

In a balanced chemical equation, the coefficients tell us the relative number of particles (atoms or molecules) that react and form products. These numbers can also be used as ratios, and the ratio stays the same no matter how many actual particles are present.

For example, in the methane combustion reaction:
$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$ the ratio is 1:2:1:2.

This means:

- 1 molecule of methane reacts with 2 molecules of oxygen
- to form 1 molecule of carbon dioxide and 2 molecules of water

But this ratio also applies to larger quantities:

- 1 dozen $\mathrm{CH_4}$ molecules reacts with 2 dozen $\mathrm{O_2}$ molecules
- 1 mole of $\mathrm{CH_4}$ reacts with 2 moles of $\mathrm{O_2}$

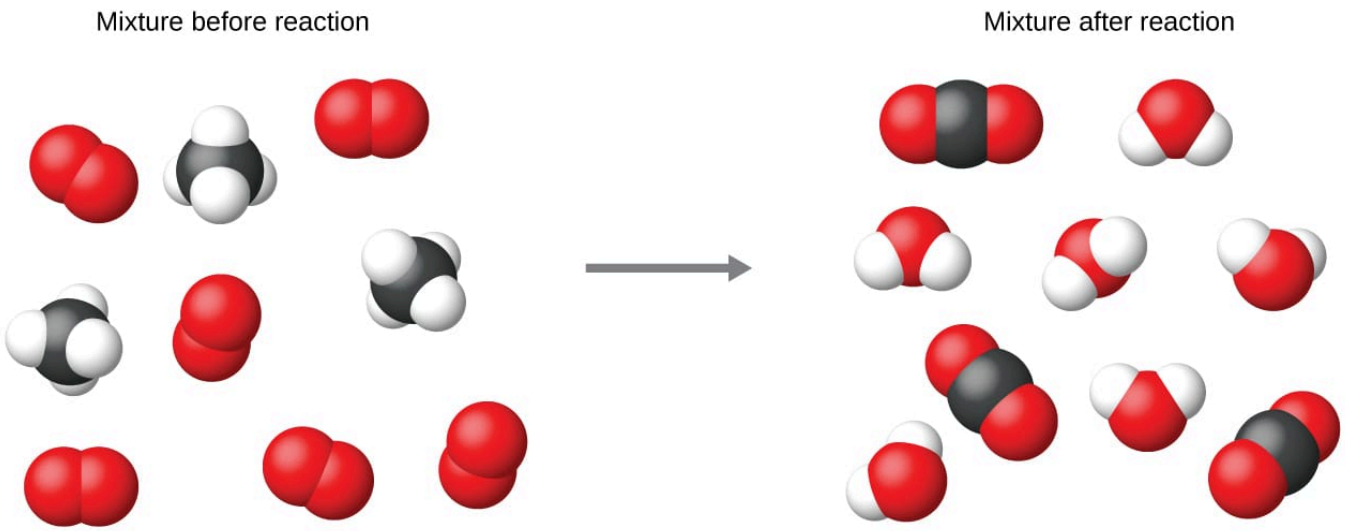


Figure $1.5.2$: Whether we are looking at individual molecules or many molecules, the ratios between reactants and products stay the same. This is the basis of stoichiometric calculations.

Balancing Equations

A balanced chemical equation shows equal numbers of each type of atom on both sides of the arrow. This is required by the law of conservation of mass; atoms are not created or destroyed in a chemical reaction, just rearranged. The chemical equation described above in Figure $1.5.1$ is balanced.

To balance an equation, you can change the coefficients (the numbers in front of chemical formulas). Subscripts inside formulas cannot be changed as this would change the identity of the substance.

Consider the following example:

Unbalanced:
$\mathrm{H_2O \longrightarrow H_2 + O_2}$

In this form:

- There are 2 hydrogen atoms on both sides
- Only 1 oxygen atom on the left and 2 on the right (not balanced)

To fix this, we can:

- Put a 2 in front of $\mathrm{H_2O}$: $\mathrm{2\,H_2O \longrightarrow H_2 + O_2}$ to give 2 oxygen atoms on each side.

That gives us 4 hydrogen atoms on the left, and only 2 on the right.

- Put a 2 in front of H_2: $2\,H_2O \longrightarrow 2\,H_2 + O_2$

Now the equation is balanced:

- 4 hydrogen atoms on both sides
- 2 oxygen atoms on both sides

Balancing chemical equations often takes a bit of trial and error. Start with the most complex formula and balance one element at a time.

Example 1.5.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide (N_2O_5).

Solution

Start with the unbalanced equation:

$$N_2 + O_2 \longrightarrow N_2O_5$$

Nitrogen is already balanced (2 atoms on each side), but the oxygen atoms are not. There are 2 oxygen atoms on the left and 5 on the right. To get the same number of oxygen atoms on both sides, multiply O_2 by 5 and N_2O_5 by 2. That gives us 10 oxygen atoms on each side:

$$N_2 + 5\,O_2 \longrightarrow 2\,N_2O_5$$

Now nitrogen is unbalanced—there are 2 nitrogen atoms on the left and 4 on the right. To fix this, place a 2 in front of N_2:

$$2\,N_2 + 5\,O_2 \longrightarrow 2\,N_2O_5$$

Now we have:

- 4 nitrogen atoms on each side
- 10 oxygen atoms on each side

The equation is balanced.

Exercise 1.5.1

Write a balanced equation for the reaction of aluminum metal (Al) with chlorine gas (Cl_2) to form aluminum chloride ($AlCl_3$).

Answer available at the end of this section.

Additional Information in Chemical Equations

Chemical equations often include physical states of the substances involved. These are shown in parentheses after each formula:

- (s) = solid
- (l) = liquid
- (g) = gas
- (aq) = aqueous (dissolved in water)

For example:
$2\,Na\,(s) + 2\,H_2O\,(l) \longrightarrow 2\,NaOH\,(aq) + H_2\,(g)$

This equation shows that solid sodium reacts with liquid water to form aqueous sodium hydroxide and hydrogen gas.

Summary

Chemical reactions involve the rearrangement of atoms to form new substances. Chemical equations use formulas and symbols to represent what happens during a reaction. Reactants appear on the left side of the arrow, and products appear on the right. Coefficients show the relative number of particles or moles involved and must be adjusted so that the number of each type of atom is the same on both sides of the equation. This reflects the law of conservation of mass. Understanding how to interpret and balance chemical equations is essential for calculating the amounts of substances involved in a reaction.

Glossary

balanced chemical equation
: A chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation
: The symbolic representation of a chemical reaction.

chemical reaction
: A process in which atoms are rearranged to form new substances with new properties.

coefficient
: A number placed in front of symbols or formulas in a chemical equation to indicate their relative amount.

law of conservation of mass
: States that atoms are neither created nor destroyed in a chemical reaction, but rather rearranged.

product
: The simplest ratio of ions in an ionic compound.

reactant
: Occurs when a metal donates one or more electrons to a nonmetal, forming oppositely charged ions.

Answers

Exercise 1.5.1

$$2\,\mathrm{Al} + 3\,\mathrm{Cl_2} \longrightarrow 2\,\mathrm{AlCl_3}$$

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1.6: Reaction Stoichiometry

Learning Objectives

- Use a balanced chemical equation to determine mole ratios between reactants and products.
- Perform stoichiometric calculations involving mass, moles, or molecules.
- Identify the limiting reactant in a chemical reaction.
- Calculate the theoretical yield of a product based on stoichiometry.
- Determine the percent yield of a reaction given actual and theoretical yields.

Balanced chemical equations represent the species involved in a chemical reaction and also the quantity of those species. The formulas identify the substances involved, and the coefficients tell us the relative number of particles or moles of each reactant and product. These quantitative relationships are called the stoichiometry of the reaction, from the Greek words stoicheion (element) and metron (measure).

Stoichiometry allows us to answer important questions such as:

- How much product can be formed from a given amount of reactant?
- How much of one reactant is needed to fully consume another?
- Which reactant will limit the amount of product?

For example, consider the synthesis of ammonia:

$$\mathrm{N_2\,(g) + 3\,H_2(g) \longrightarrow 2\,NH_3\,(g)}$$

This equation tells us that 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia. These mole ratios can be used as conversion factors to relate the amounts of any substances in the equation:

$$\frac{2\,\mathrm{mol\,NH_3}}{3\,\mathrm{mol\,H_2}},\quad \frac{3\,\mathrm{mol\,H_2}}{1\,\mathrm{mol\,N_2}},\quad \frac{2\,\mathrm{mol\,NH_3}}{1\,\mathrm{mol\,N_2}},\,\mathrm{etc.}$$

We'll use these ratios throughout this section to calculate masses, moles, and molecular quantities in chemical reactions.

Example 1.6.1: Moles of Reactant Required in a Reaction

How many moles of $\mathrm{I_2}$ are required to react with 0.429 mol of Al according to the following equation (Figure 1.6.1)?

$$\mathrm{2\,Al\,(s) + 3\,I_2\,(s) \longrightarrow 2\,AlI_3\,(s)}$$

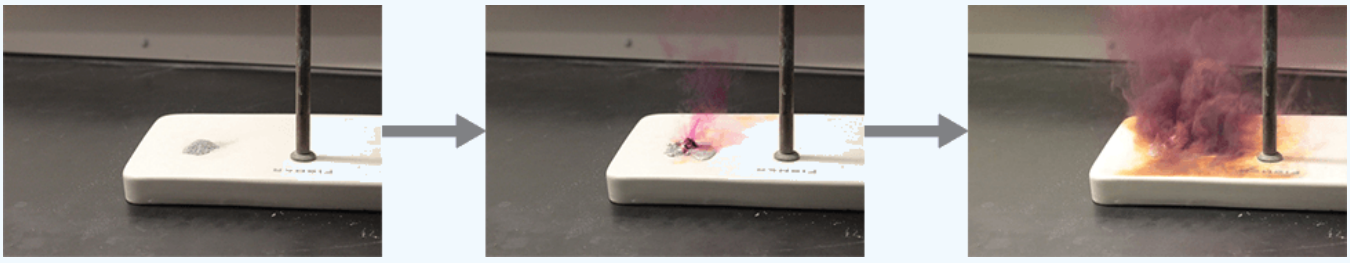


Figure 1.6.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Solution

We use the stoichiometric ratio from the balanced chemical equation (2 mol Al = 3 mol $\mathrm{I_2}$) to convert moles of aluminum to moles of iodine :

$$\text{mol I}_2 = 0.429 \cancel{\text{ mol Al}} \left(\frac{3 \text{ mol I}_2}{2 \cancel{\text{ mol Al}}} \right)$$
$$= 0.644 \text{ mol I}_2$$

Exercise 1.6.1

How many moles of Ca(OH)_2 are required to react with 1.36 mol of H_2PO_4 to produce $\text{Ca}_3(\text{PO}_4)_2$ according to the following equation?

$$2\,\text{H}_3\text{PO}_4\,(\text{aq}) + 3\,\text{Ca(OH)}_2\,(\text{aq}) \longrightarrow \text{Ca}_3(\text{PO}_4)_2\,(\text{s}) + 6\,\text{H}_2\text{O}\,(\text{l})$$

Answer available at the end of this section.

Example 1.6.2: 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?

$$\text{C}_3\text{H}_8 + 5\,\text{O}_2 \longrightarrow 3\,\text{CO}_2 + 4\,\text{H}_2\text{O}$$

Solution

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8}$$

We first calculate the number of moles of CO_2 produced:

$$0.75 \text{ mol C}_3\text{H}_8 \left(\frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} \right) = 2.25 \text{ mol CO}_2$$

Next, we convert moles of CO_2 to molecules using Avogadro's number (6.022×10^{23} particles = 1 mol):

$$2.25 \text{ mol CO}_2 \left(\frac{6.022 \times 10^{23} \text{ CO}_2 \text{ molecules}}{\text{mol CO}_2} \right) = 1.4 \times 10^{24} \text{ CO}_2 \text{ molecules}$$

Or the calculation can be done in a single step:

$$0.75 \text{ mol C}_3\text{H}_8 \left(\frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} \right) \left(\frac{6.022 \times 10^{23} \text{ CO}_2 \text{ molecules}}{\text{mol CO}_2} \right) = 1.4 \times 10^{24} \text{ CO}_2 \text{ molecules}$$

Exercise 1.6.2

How many NH_3 molecules are produced by the reaction of 4.0 mol of Ca(OH)_2 according to the following equation:

$$(\text{NH}_4)_2\text{SO}_4 + \text{Ca(OH)}_2 \longrightarrow 2\,\text{NH}_3 + \text{CaSO}_4 + 2\,\text{H}_2\text{O}$$

Answer available at the end of this section.

These examples show how easily balanced chemical equations let us relate the amounts of substances in a reaction. However, we can't directly count atoms and molecules in the lab. Instead, stoichiometry is usually based on mass, a quantity we can measure. To connect mass with the number of particles involved, we use molar mass (also called molecular weight), which allows us to convert between grams and moles.

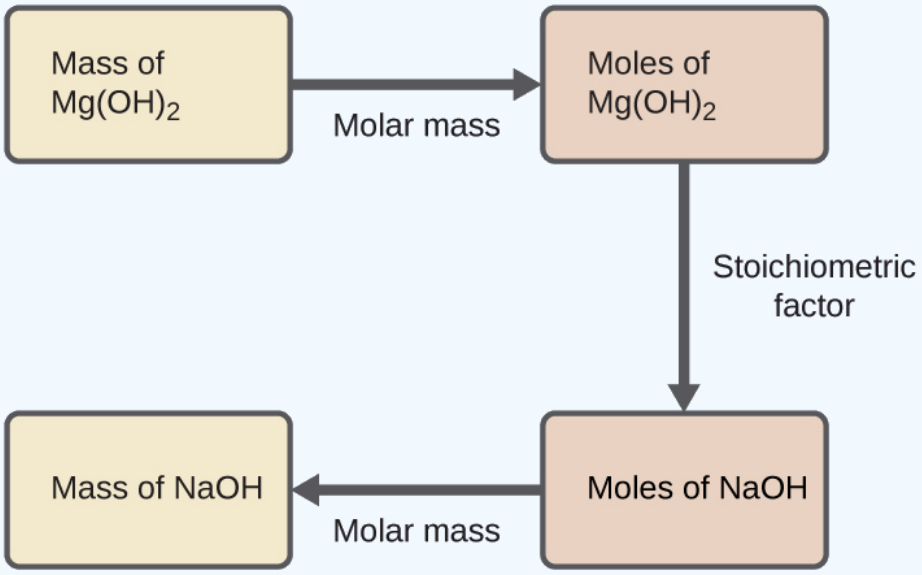
Example 1.6.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $\mathrm{Mg(OH)_2}$] by the following reaction?

$$\mathrm{MgCl_2\,(aq) + 2\,NaOH\,(aq) \longrightarrow Mg(OH)_2\,(s) + 2\,NaCl\,(aq)}$$

Solution

We are given the mass of a product and asked to find the mass of a reactant. Because the balanced chemical equation relates numbers of particles (in moles), we cannot work directly in grams. Instead, we must first convert the given mass to moles, use the mole ratio from the balanced equation to relate the two substances, and then convert back to mass. The required steps are summarized in the following flowchart:



$$16\ \mathrm{g\ Mg(OH)_2}\left(\frac{1\ \mathrm{mol\ Mg(OH)_2}}{58.3\ \mathrm{g\ Mg(OH)_2}}\right)\left(\frac{2\ \mathrm{mol\,NaOH}}{1\,\mathrm{mol\,Mg(OH)_2}}\right)\left(\frac{40.0\,\mathrm{g\,NaOH}}{\mathrm{mol\,NaOH}}\right) = 22\,\mathrm{g\,NaOH}$$

Exercise 1.6.3

What mass of gallium oxide, $\mathrm{Ga_2O_3}$, can be prepared from 29.0 g of gallium metal? The equation for the reaction is:

$$\mathrm{4\,Ga + 3\,O_2 \longrightarrow 2\,Ga_2O_3}$$

Answer available at the end of this section.

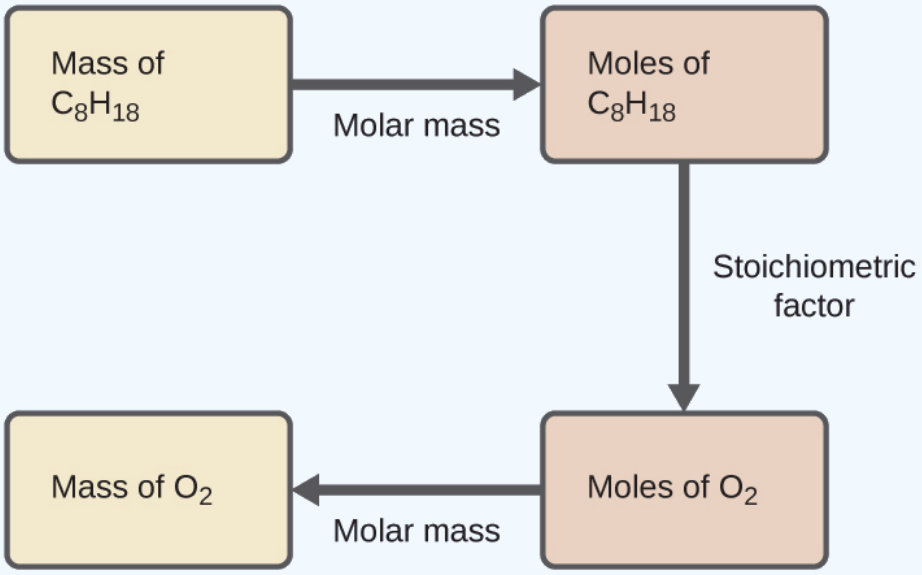
Example 1.6.4: Relating Masses of Reactants

What mass of oxygen gas, $\mathrm{O_2}$, from the air is consumed in the combustion of 702 g of octane, $\mathrm{C_8H_{18}}$, one of the principal components of gasoline?

$$\mathrm{2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O}$$

Solution

The approach required here is the same as for the Example 1.6.3, differing only in that the provided and requested masses are both for reactant species.



We convert the mass of octane to moles, use the mole ratio from the balanced equation, and then convert to grams of O_2:

$$702\ \text{g}\ \text{C}_8\text{H}_{18} \times \frac{1\ \text{mol}\ \text{C}_8\text{H}_{18}}{114.23\ \text{g}\ \text{C}_8\text{H}_{18}} \times \frac{25\ \text{mol}\ \text{O}_2}{2\ \text{mol}\ \text{C}_8\text{H}_{18}} \times \frac{32.00\ \text{g}\ \text{O}_2}{\text{mol}\ \text{O}_2} = 2.46 \times 10^3\ \text{g}\ \text{O}_2$$

Exercise 1.6.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation?

$$\text{Fe}_2\text{O}_3 + 3\,\text{CO} \longrightarrow 2\,\text{Fe} + 3\,\text{CO}_2$$

Answer available at the end of this section.

These examples show just a few types of stoichiometric calculations. Many variations are possible, depending on what quantities are given and what is being asked (such as volumes, concentrations, or masses). But all stoichiometry problems share a key feature: the use of stoichiometric ratios from a balanced chemical equation.

Chemistry in Everyday Life: Airbags

Airbags (Figure 1.6.2) have been a standard automotive safety feature since the 1990s. For an airbag to work effectively, it must inflate rapidly with the correct volume of gas during a collision. This is often achieved using explosive decomposition of sodium azide, NaN_3:

$$2\,\text{NaN}_3\,(\text{s}) \longrightarrow 3\,\text{N}_2\,(\text{g}) + 2\,\text{Na}\,(\text{s})$$

When crash sensors detect an impact, an electrical current triggers the decomposition of a carefully measured amount of NaN_3. The reaction produces nitrogen gas almost instantly, inflating the airbag in just 0.03 to 0.1 seconds. The amount of sodium azide used must be calculated precisely to ensure enough nitrogen is produced to fill the airbag. For example, about 100 g of NaN_3 generates roughly 50 L of N_2 gas.



Figure 1.6.2: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as stoichiometric amounts. All the previous exercises involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered in which reactants are not present in stoichiometric amounts.

Limiting Reactant

Consider a food analogy, making grilled cheese sandwiches (Figure 1.6.3):

$$1 \text{ slice of cheese} + 2 \text{ slices of bread} \longrightarrow 1 \text{ sandwich}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, cheese is the limiting reactant as it determines how many sandwiches can be made. Bread is the excess reactant, since some is left over after the cheese is used up.

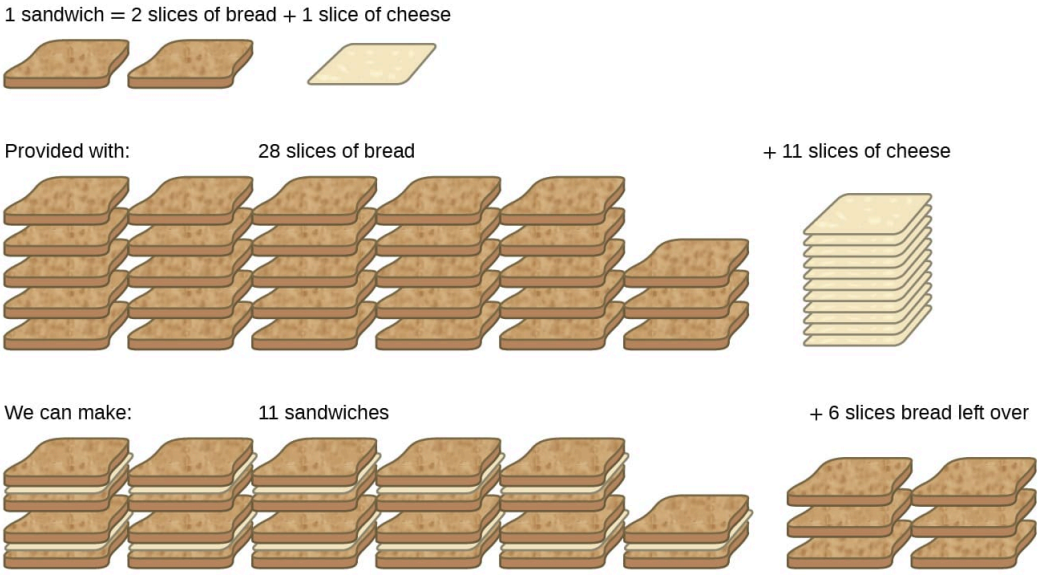


Figure 1.6.3: Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical reaction: the formation of hydrogen chloride from hydrogen and chlorine gas.

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

The balanced equation shows that hydrogen and chlorine react in a 1:1 molar ratio. If the reactants are present in any other ratio, one will run out before the other. The reactant that is completely used up first limits the amount of product formed and is called the limiting reactant. The other reactant is present in excess.

To identify the limiting reactant, we compare the moles of each reactant available to the stoichiometric ratio from the balanced equation. For example, suppose we mix 6 moles of $\mathrm{H_2}$ and 4 moles of $\mathrm{Cl_2}$. This is a 3:2 (or 1.5:1) ratio, which is greater than the required 1:1 ratio. So hydrogen is in excess, and chlorine is the limiting reactant. The 4 moles of $\mathrm{Cl_2}$ will react completely with 4 of the 6 moles of $\mathrm{H_2}$, leaving 2 moles of hydrogen unreacted.

Another way to identify the limiting reactant is to calculate how much product each reactant would produce, and determine which produces less. The one that forms less product is the limiting reactant.

Using the amounts above:

$$\mathrm{mol\,HCl\,produced} = 6\,\mathrm{mol\,H_2} \times \frac{2\,\mathrm{mol\,HCl}}{1\,\mathrm{mol\,H_2}} = 12\,\mathrm{mol\,HCl}$$

$$\mathrm{mol\,HCl\,produced} = 4\,\mathrm{mol\,Cl_2} \times \frac{2\,\mathrm{mol\,HCl}}{1\,\mathrm{mol\,Cl_2}} = 8\,\mathrm{mol\,HCl}$$

Only 8 moles of HCl will form, because the chlorine will run out. This confirms that chlorine is the limiting reactant, and hydrogen is in excess (Figure $1.6.4$).

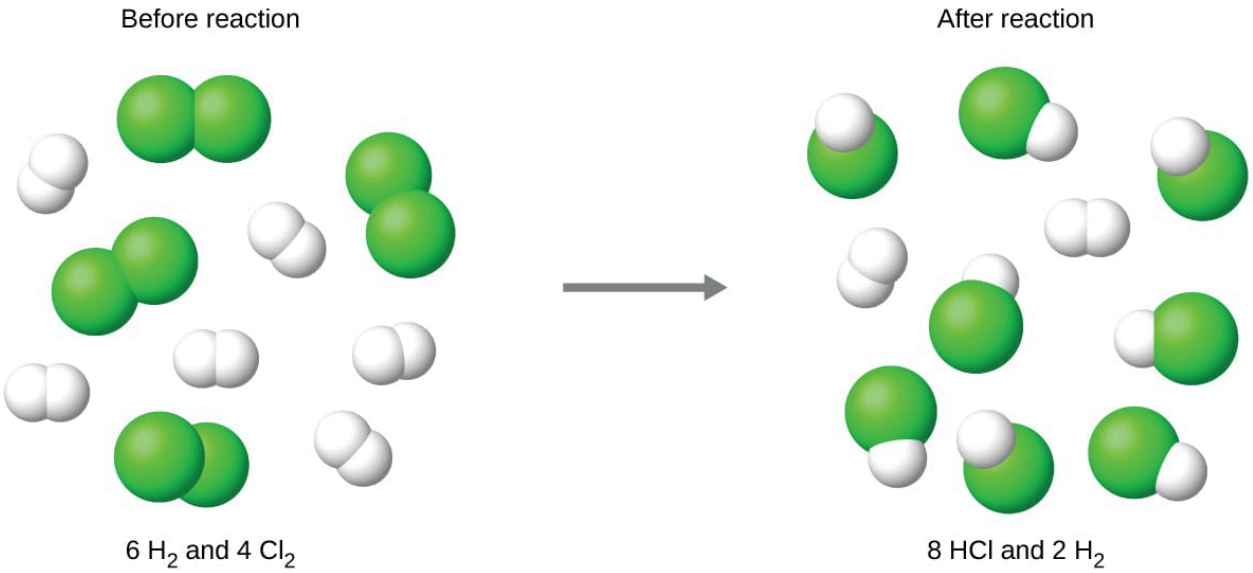


Figure $1.6.4$: When $\mathrm{H_2}$ and $\mathrm{Cl_2}$ are combined in nonstoichiometric amounts, one reactant limits the amount of HCl produced. Here, hydrogen is in excess and chlorine is the limiting reactant.

Link to Learning

View this interactive simulation illustrating the concepts of limiting and excess reactants.

Example 1.6.5: Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\,\mathrm{Si}\,(\mathrm{s}) + 2\,\mathrm{N_2}\,(\mathrm{g}) \longrightarrow \mathrm{Si_3N_4}\,(\mathrm{s})$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of $\mathrm{N_2}$ react?

How many grams of $\mathrm{Si_3N_4}$ are formed?

Solution

Strategy:

1. Convert the mass of each reactant to moles.
2. Use mole ratios to determine how many moles of product could form from each reactant if they reacted completely.
3. Identify the limiting reactant, the one that produces less product.
4. Use that amount of product (in moles) to calculate the mass formed.

1. Convert mass to moles:

$$2.00\ \mathrm{g\ Si}\left(\frac{\mathrm{mol}}{28.09\ \mathrm{g}}\right) = 0.0712\ \mathrm{mol\ Si}$$

$$1.50\ \mathrm{g N_2}\left(\frac{\mathrm{mol}}{28.01\ \mathrm{g}}\right) = 0.0536\ \mathrm{mol\ N_2}$$

2. Determine how many moles of $\mathrm{Si_3N_4}$ each reactant could produce:

$$0.0712\ \mathrm{mol\ Si}\left(\frac{\mathrm{mol\ Si_3N_4}}{3\ \mathrm{mol\ Si}}\right) = 0.0237\ \mathrm{mol\ Si_3N_4}$$

$$0.0536\ \mathrm{mol\ N_2}\left(\frac{\mathrm{mol\ Si_3N_4}}{2\ \mathrm{mol\ N_2}}\right) = 0.0268\ \mathrm{mol\ Si_3N_4}$$

3. Identify the limiting reactant:

Since Si produces less product, it would run out first and is the limiting reactant.

4. Calculate the mass of product formed (based on moles formed from limiting reactant):

$$0.0237\ \mathrm{mol\ Si_3N_4}\left(\frac{140.28\ \mathrm{g}}{\mathrm{mol}}\right) = 3.32\ \mathrm{g\ Si_3N_4}$$

Exercise 1.6.5

Iron(III) oxide reacts with carbon monoxide gas to produce solid iron and carbon dioxide gas:

$$\mathrm{Fe_2O_3}\,(\mathrm{s}) + 3\,\mathrm{CO}\,(\mathrm{g}) \longrightarrow 2\,\mathrm{Fe}\,(\mathrm{s}) + 3\,\mathrm{CO_2}\,(\mathrm{g})$$

If 6.50 g of $\mathrm{Fe_2O_3}$ reacts with 3.00 g of CO:

Which reactant is limiting?

How many grams of iron (Fe) are produced?

Answer available at the end of this section.

Percent Yield

The theoretical yield is the amount of product that should be produced in a reaction, based on stoichiometric calculations from a balanced chemical equation. In practice, the amount of product actually obtained, the actual yield, is often less than the theoretical yield.

This difference can happen for many reasons:

- Some reactions are incomplete (like those involving weak acids or bases).
- Some reactions have side reactions that form unwanted products.
- Some products are difficult to isolate or recover completely.

To express how efficiently a reaction produced the desired product, we calculate the percent yield:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{1.6.1}$$

Both actual and theoretical yields can be expressed in grams, moles, volume, or any other appropriate unit. As long as the units are the same, they will cancel when calculating percent yield.

Example 1.6.6: Calculation of Percent Yield

When 1.274 g of copper(II) sulfate reacts with excess zinc metal, 0.392 g of copper metal is obtained according to the following equation:

$$\mathrm{CuSO_4(aq) + Zn(s) \longrightarrow Cu(s) + ZnSO_4(aq)}$$

What is the percent yield?

Solution

Since zinc is in excess, copper(II) sulfate is the limiting reactant. We can calculate the theoretical yield of copper using the stoichiometry from the balanced reaction:

$$1.274\ \text{g CuSO}_4 \times \frac{1\ \text{mol CuSO}_4}{159.62\ \text{g CuSO}_4} \times \frac{1\ \text{mol Cu}}{1\ \text{mol CuSO}_4} \times \frac{63.55\ \text{g Cu}}{1\ \text{mol Cu}} = 0.5072\ \text{g Cu}$$

Using the actual and theoretical yields, we calculate the percent yield:

$$\begin{aligned}\text{percent yield} &= \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100\% \\ &= \left(\frac{0.392\ \text{g Cu}}{0.5072\ \text{g Cu}}\right) \times 100\% \\ &= 77.3\%\end{aligned}$$

Exercise 1.6.6

What is the percent yield of a reaction that produces 12.5 g of the gas Freon $\mathrm{CF_2Cl_2}$ from 32.9 g of $\mathrm{CCl_4}$ and excess HF?

$$\mathrm{CCl_4 + 2\,HF \longrightarrow CF_2Cl_2 + 2\,HCl}$$

Answer available at the end of this section.

Summary

A balanced chemical equation describes the stoichiometry of a reaction, the quantitative relationships between reactants and products. The coefficients in the equation represent mole ratios that can be used to calculate masses, molar amounts, and other

measurable properties of the substances involved.

If one or more reactants are present in less than stoichiometric amounts, the limiting reactant determines the maximum amount of product that can form. The actual yield is the amount of product actually obtained, which is often less than the theoretical yield predicted by stoichiometry. The percent yield expresses how much product was obtained relative to the theoretical maximum:

$$\text{percent yield } = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Glossary

actual yield
: The amount of product formed in a reaction.

excess reactant
: The reactant present in an amount greater than required by the reaction stoichiometry.

limiting reactant
: The reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated.

mole ratio
: Unit conversation factor that relates the number of moles of substances in a balanced chemical equation.

percent yield
: Measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield.

stoichiometry
: The quantitative relationships between substances in a balanced chemical reaction.

theoretical yield
: The amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry.

Answers

Exercise 1.6.1

$$1.36 \cancel{\text{ mol } H_3PO_4} \left(\frac{3 \text{ mol } Ca(OH)_2}{2 \cancel{\text{ mol } H_3PO_4}} \right) = 2.04 \text{ mol } Ca(OH)_2$$

Exercise 1.6.2

$$4.0 \text{ mol } Ca(OH)_2 \left(\frac{2 \text{ mol } NH_3}{1 \text{ mol } Ca(OH)_2} \right) \left(\frac{6.022 \times 10^{23} \text{ } NH_3 \text{ molecules}}{\text{mol } NH_3} \right) = 4.8 \times 10^{24} \text{ } NH_3 \text{ molecules}$$

Exercise 1.6.3

$$29.0 \text{ g Ga} \left(\frac{1 \text{ mol Ga}}{69.72 \text{ g Ga}} \right) \left(\frac{2 \text{ mol } Ga_2O_3}{4 \text{ mol Ga}} \right) \left(\frac{187.44 \text{ g } Ga_2O_3}{\text{mol } Ga_2O_3} \right) = 39.0 \text{ g } Ga_2O_3$$

Exercise 1.6.4

$$25.13 \text{ g } Fe_2O_3 \times \frac{1 \text{ mol } Fe_2O_3}{159.69 \text{ g } Fe_2O_3} \times \frac{3 \text{ mol CO}}{1 \text{ mol } Fe_2O_3} \times \frac{28.01 \text{ g CO}}{\text{mol CO}} = 13.22 \text{ g CO}$$

Exercise 1.6.5

1. Convert mass to moles:

$$6.50 \text{ g } Fe_2O_3 \left(\frac{\text{mol}}{159.69 \text{ g}} \right) = 0.0407 \text{ mol } Fe_2O_3$$

$$3.00 \text{ g CO} \left(\frac{\text{mol}}{28.01 \text{ g}} \right) = 0.107 \text{ mol CO}$$

2. Determine how many moles of Fe each reactant could produce:

$$0.0407 \text{ mol } Fe_2O_3 \left(\frac{2 \text{ mol Fe}}{\text{mol } Fe_2O_3} \right) = 0.0814 \text{ mol Fe}$$

$$0.107 \text{ mol CO} \left(\frac{2 \text{ mol Fe}}{3 \text{ mol CO}} \right) = 0.0713 \text{ mol Fe}$$

3. Identify the limiting reactant:

Since CO produces less product, it would run out first and is the limiting reactant.

4. Calculate the mass of product formed (based on moles formed from limiting reactant):

$$0.0713 \text{ mol Fe} \left(\frac{55.85 \text{ g}}{\text{mol}} \right) = 3.98 \text{ g Fe}$$

Exercise 1.6.6

First, calculate the theoretical yield of CF_2Cl_2 from the given amount of CCl_4. Since HF is in excess, CCl_4 is the limiting reactant.

Molar mass of CCl_4 = 153.82 g/mol
Molar mass of CF_2Cl_2 = 120.91 g/mol

$$32.9 \text{ g } CCl_4 \times \frac{1 \text{ mol } CCl_4}{153.82 \text{ g } CCl_4} \times \frac{1 \text{ mol } CF_2Cl_2}{1 \text{ mol } CCl_4} \times \frac{120.91 \text{ g } CF_2Cl_2}{1 \text{ mol } CF_2Cl_2} = 25.9 \text{ g } CF_2Cl_2$$

Now calculate the percent yield using the actual yield (12.5 g):

$$\text{percent yield} = \left(\frac{12.5 \text{ g}}{25.9 \text{ g}} \right) \times 100\% = 48.3\%$$

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1.7: Molarity and Solution Stoichiometry

Learning Objectives

- Describe the components of a solution and calculate its molarity.
- Perform dilution calculations.
- Use molarity and balanced chemical equations to solve stoichiometry problems involving reactions in solution.

Whether it's disinfecting drinking water, administering intravenous medications, or analyzing blood samples, many important chemical processes happen in solution. Understanding how to describe and control the amount of a substance dissolved in a liquid is essential for applying chemistry in real-world contexts.

Chemists express the concentration of a solution using molarity (M), the number of moles of solute per litre of solution. By combining this with balanced chemical equations, we can perform solution stoichiometry calculations to determine how much of each substance reacts or forms in an aqueous process. In this section, you'll learn how to calculate molarity, perform dilutions, and use volume and concentration in stoichiometric problem-solving.

Solutions

A solution is a homogeneous mixture, meaning its composition is uniform throughout. Most solutions consist of a solvent, the substance present in the greatest amount (often water), and one or more solutes, which are dissolved in the solvent. The concentration of a solute tells us how much of it is present in a given amount of solution. Solute concentrations are often described with qualitative terms such as dilute (relatively low concentration) and concentrated (relatively high concentration).

In chemistry, concentration is most commonly expressed using molarity (M):

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Example 1.7.1: Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molarity of sucrose in the beverage?

Solution

Since both the amount of solute (in moles) and the volume of solution are given, we can use the definition of molarity:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

First, convert the volume from millilitres to litres:

$$355\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 0.355\ \text{L}$$

Now calculate the molarity:

$$\frac{0.133\ \text{mol}}{0.355\ \text{L}} = 0.375\ \text{M}$$

Exercise 1.7.1

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?

Answer available at the end of this section.

Example 1.7.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (in moles) is contained in a sip (10 mL) of the soft drink from Example 1.7.1?

Solution

We can rearrange the definition of molarity to solve for the number of moles of sugar. From Example 1.7.1, the molarity is 0.375 M:

$$\begin{aligned} M &= \frac{\text{mol solute}}{L \text{ solution}} \\ \text{mol solute} &= M \times L \text{ solution} \\ &= 0.375 \frac{\text{mol sugar}}{L} \left(10\,\text{mL} \times \frac{1\,\text{L}}{1000\,\text{mL}}\right) \\ &= 0.004\,\text{mol sugar} \end{aligned}$$

Exercise 1.7.2

What volume (mL) of the sweetened tea described in Exercise 1.7.1 contains the same amount of sugar (in moles) as 10 mL of the soft drink in this example?

Answer available at the end of this section.

Example 1.7.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 1.7.1) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500 L vinegar solution contains 25.2 g of acetic acid. What is the molarity of the acetic acid solution?



Figure 1.7.1: Distilled white vinegar is a solution of acetic acid in water.

Solution

Since the mass of solute is provided instead of its molar amount, use the solute's molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\,\text{g}\,\text{CH}_3\text{CO}_2\text{H}\left(\frac{\text{mol}\,\text{CH}_3\text{CO}_2\text{H}}{60.052\,\text{g}\,\text{CH}_3\text{CO}_2\text{H}}\right)}{0.500\,\text{L solution}} = 0.839\,\text{M}$$

Exercise 1.7.3

Calculate the molarity of 6.52 g of CoCl_2 (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer available at the end of this section.

Example 1.7.4: Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30 M solution?

Solution

$$\begin{aligned} M &= \frac{\text{mol solute}}{L\text{ solution}} \\ \text{mol solute} &= M \times L\text{ solution} \\ &= 5.30\frac{\text{mol NaCl}}{\text{L}} \times 0.250L \\ &= 1.325\,\text{mol NaCl} \end{aligned}$$

Finally, this molar amount is used to find the mass of NaCl:

$$1.325\,\text{mol NaCl} \times \frac{58.44\,\text{g NaCl}}{1\,\text{mol NaCl}} = 77.4\,\text{g NaCl}$$

Exercise 1.7.4

How many grams of $\mathrm{CaCl_2}$ (110.98 g/mol) are contained in 250.0 mL of a 0.200 M solution of calcium chloride?

Answer available at the end of this section.

Example 1.7.5: Determining the Volume of Solution Containing a Given Mass of Solute

In Example 1.7.3, the molarity of acetic acid in white vinegar was determined to be 0.839 M. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:

$$\text{g solute} \times \left(\frac{\text{mol solute}}{\text{g solute}}\right) \times \left(\frac{\text{L solution}}{\text{mol solute}}\right) = \text{L solution}$$

$$75.6\,\text{g}\,\mathrm{CH_3CO_2H}\left(\frac{\text{mol}\,\mathrm{CH_3CO_2H}}{60.05\,\text{g}}\right)\left(\frac{\text{L solution}}{0.839\,\text{mol}\,\mathrm{CH_3CO_2H}}\right) = 1.50\,\text{L solution}$$

Exercise 1.7.5

What volume of a 1.50 M KBr solution contains 66.0 g KBr?

Answer available at the end of this section.

Dilution of Solutions

Dilution is the process of reducing the concentration of a solution by adding more solvent. For example, a solution of copper nitrate becomes more dilute if you add water to it. The concentration decreases because the same number of solute particles is now dispersed in a larger volume (Figure 1.7.2).

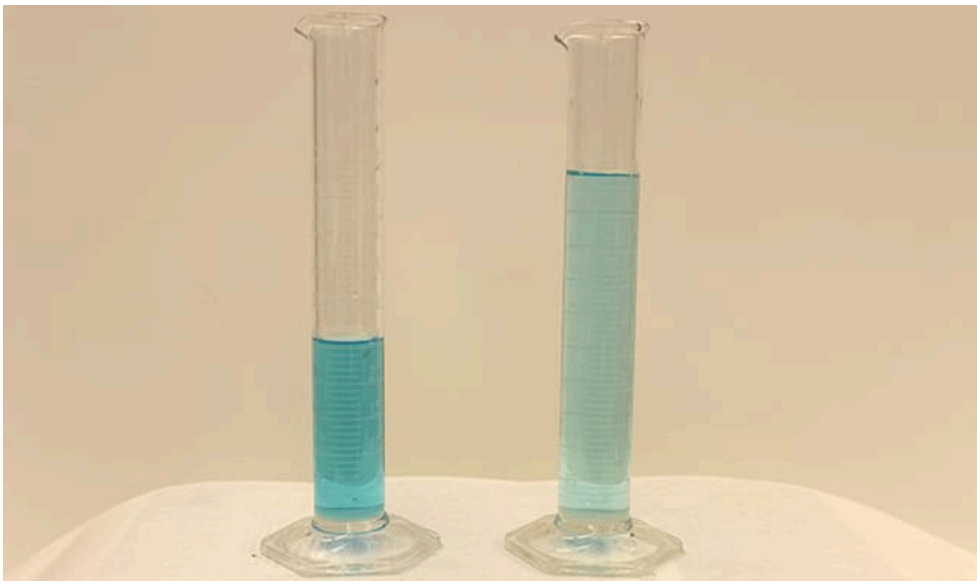


Figure 1.7.2: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)

Dilution is often used in the lab or in real-world applications to prepare a solution of a desired concentration from a more concentrated one, called a stock solution. For example, commercial pesticides are typically sold in concentrated form and diluted before use. Laboratory reagents are commonly prepared in this way as well.

The key idea in any dilution is that the amount of solute stays the same; only the volume changes. If you know the volume and concentration of the original solution and the final volume you want, you can calculate the final concentration using the definition of molarity:

$$\text{moles of solute} = M \times V$$

Because the number of moles of solute does not change during a dilution, we can write:

$$\text{moles before} = \text{moles after}$$
$$M_1V_1 = M_2V_2$$

This relationship is useful for thinking about dilution conceptually: the same number of solute particles is now present in a greater volume, so the molarity decreases.

Example 1.7.6: Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00 M solution of copper nitrate, $\mathrm{Cu(NO_3)_2}$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

The number of moles of $\mathrm{Cu(NO_3)_2}$ stays the same, but they are now dispersed in a larger volume of solution.

Find moles before dilution:

$$5.00\,\frac{\text{mol}}{\text{L}}(0.850\,\text{L}) = 4.25\,\text{mol}$$

Use new volume to find molarity after dilution:

$$\frac{4.25\,\text{mol}}{1.80\,\text{L}} = 2.36\,\text{M}$$

Or using $M_1V_1 = M_2V_2$:

$$M_2 = \frac{M_1V_1}{V_2} = \frac{(5.00\ \frac{\text{mol}}{\text{L}})(0.850\,\text{L}))}{1.80\,\text{L}} = 2.36\,\text{M}$$

Exercise 1.7.6

What is the molarity of the solution that results from diluting 25.0 mL of a 2.04 M solution of CH_3OH to 500.0 mL?

Answer available at the end of this section.

Example 1.7.7: Volume of a Diluted Solution

What volume of 0.12 M HBr can be prepared from 0.011 L of 0.45 M HBr?

Solution

First, calculate the number of moles of HBr in the original (more concentrated) solution:

$$0.45\,\frac{\text{mol}}{\text{L}}(0.011\,\text{L}) = 0.00495\,\text{mol}$$

Now calculate the volume of the diluted solution that would contain this amount of HBr at a molarity of 0.12 M:

$$0.00495\,\text{mol}\left(\frac{\text{L}}{0.12\,\text{mol}}\right) = 0.041\,\text{L} = 41\,\text{mL}$$

Or using $M_1V_1 = M_2V_2$:

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(0.45\,\text{M})(0.011\,\text{L}))}{0.12\,\text{M}} = 0.041\,\text{L}$$

Exercise 1.7.7

A laboratory experiment calls for 0.125 M HNO_3. What volume of 0.125 M HNO_3 can be prepared from 0.250 L of 1.88 M HNO_3?

Answer available at the end of this section.

Example 1.7.8: 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?

Solution

We are given the final volume and molarity, so start by calculating the number of moles of KOH needed after dilution:

$$0.100\,\frac{\text{mol}}{\text{L}}(5.00\,\text{L}) = 0.500\,\text{mol}$$

Now calculate the volume of the concentrated solution that contains this amount of solute:

$$0.500\,\text{mol}\left(\frac{\text{L}}{1.59\,\text{mol}}\right) = 0.314\,\text{L} = 314\,\text{mL}$$

Or using $M_1V_1 = M_2V_2$:

$$V_1 = \frac{M_2V_2}{M_1} = \frac{(0.100\,\text{M})(5.00\,\text{L}))}{1.59\,\text{M}} = 0.314\,\text{L}$$

Exercise 1.7.8

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?

Answer available at the end of this section.

Solution Stoichiometry

From the molarity of a solution, you can calculate how many moles of solute are present in a given volume. This allows us to use solution data in stoichiometric calculations just like we use mass or mole data in other types of reactions.

The key idea is that volume and molarity together give us moles:

$$\text{moles of solute} = M \times V$$

With the number of moles known, we can use balanced chemical equations to relate one substance to another through mole ratios, just as in any other stoichiometry problem.

This approach is especially useful for reactions involving aqueous solutions, such as acid-base neutralizations, precipitation reactions, and redox reactions. In the examples that follow, you'll use molarity and volume to calculate how much reactant is needed or how much product forms during a chemical reaction in solution.

Example 1.7.9

What volume of 0.200 M $NaOH$ is needed to completely react with 25.0 mL of 0.150 M H_2SO_4?

$$H_2SO_4\,(aq) + 2\,NaOH\,(aq) \longrightarrow Na_2SO_4\,(aq) + 2\,H_2O\,(l)$$

Solution

1. Find moles of H_2SO_4 from volume and molarity:

$$0.150\,\frac{\text{mol}}{\text{L}} \times 0.0250\,\text{L} = 0.00375\,\text{mol}\ H_2SO_4$$

2. Use mole ratio to find moles of $NaOH$ needed:

$$0.00375\,\text{mol}\ H_2SO_4 \times \frac{2\,\text{mol}\ NaOH}{1\,\text{mol}\ H_2SO_4} = 0.00750\,\text{mol}\ NaOH$$

3. Use molarity to find volume of $NaOH$ needed:

$$\frac{0.00750\,\text{mol}}{0.200\,\frac{\text{mol}}{\text{L}}} = 0.0375\,\text{L} = 37.5\,\text{mL}$$

Exercise 1.7.9

What volume of 0.300 M Na_3PO_4 is required to completely react with 20.0 mL of 0.250 M $CaCl_2$?
The balanced equation is:

$$3\,\mathrm{CaCl_2\,(aq)} + 2\,\mathrm{Na_3PO_4\,(aq)} \longrightarrow \mathrm{Ca_3(PO_4)_2\,(s)} + 6\,\mathrm{NaCl\,(aq)}$$

Answer available at the end of this section.

Summary

Solutions are homogeneous mixtures consisting of one or more solutes dissolved in a solvent. The concentration of a solution is most commonly expressed as molarity (M), defined as the number of moles of solute per litre of solution:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

In a dilution, solvent is added to a solution, decreasing its concentration without changing the amount of solute. The key relationship is:

$$M_1V_1 = M_2V_2$$

where M_1 and V_1 are the molarity and volume of the concentrated solution, and M_2 and V_2 are those of the diluted solution.

Knowing the molarity of a solution allows you to solve stoichiometry problems involving reactions in solution, by converting volumes to moles using molarity and applying mole ratios from balanced chemical equations.

Glossary

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
: The process of adding solvent to a solution in order to lower the concentration of solutes.

homogeneous mixture
: A combination of substances with a composition that is uniform throughout.

molarity (M)
: A unit of concentration, defined as the number of moles of solute dissolved in 1 litre of solution.

solute
: Solution component present in a concentration less than that of the solvent.

solution
: A homogeneous mixture consisting of one or more solutes dissolved in a solvent.

solvent
: Solution component present in a concentration that is higher relative to other components.

stock solution
: A solution of a desired concentration diluted from a more concentrated one.

Answers

Exercise 1.7.1

$$\frac{0.01\text{ mol}}{0.200\text{ L}} = 0.05\text{ M}$$

Exercise 1.7.2

The molarity of the tea in Exercise 1.7.1 is 0.05 M. To give 0.004 moles of sugar:

$$\begin{aligned} M &= \frac{\text{mol solute}}{L \text{ solution}} \\ \text{L solution} &= \frac{\text{mol solute}}{M} \\ &= \frac{0.004\,\text{mol sugar}}{0.05 \frac{\text{mol sugar}}{L}} \\ &= 0.08\,\text{L} = 80\,\text{mL} \end{aligned}$$

Showing and cancelling units is very helpful in these problems.

Exercise 1.7.3

$$\frac{6.52\,\text{g}\left(\frac{\text{mol}}{128.9\,\text{g}}\right)}{75.0\,\text{mL}\left(\frac{\text{L}}{1000\,\text{mL}}\right)} = 0.674\,\text{M}$$

Exercise 1.7.4

$$0.200\,\frac{\text{mol}}{\text{L}}(0.2500\,\text{L}) = 0.0500\,\text{mol}\,\text{CaCl}_2$$

$$0.0500\,\text{mol}\,\text{CaCl}_2\left(\frac{110.98\,\text{g}}{\text{mol}}\right) = 5.55\,\text{g}\,\text{CaCl}_2$$

Exercise 1.7.5

$$66.0\,\text{g}\left(\frac{\text{mol}}{119.00\,\text{g}}\right)\left(\frac{\text{L}}{1.50\,\text{mol}}\right) = 0.370\,\text{L}$$

Exercise 1.7.6

$$\frac{\left(2.04\,\frac{\text{mol}}{\text{L}}(0.0250\,\text{L})\right)}{0.500\,\text{L}} = 0.102\,\text{M}$$

Exercise 1.7.7

$$1.88\,\frac{\text{mol}}{\text{L}}(0.250\,\text{L}) = 0.470\,\text{mol}$$

$$0.470\,\text{mol}\left(\frac{\text{L}}{0.125\,\text{mol}}\right) = 3.76\,\text{L}$$

Or using $M_1V_1 = M_2V_2$:

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(1.88\,\text{M})(0.250\,\text{L}))}{0.125\,\text{M}} = 3.76\,\text{L}$$

Exercise 1.7.8

$$3.00\,\frac{\text{mol}}{\text{L}}(0.0500\,\text{L}) = 0.150\,\text{mol}$$

$$0.150\,\text{mol}\left(\frac{\text{L}}{0.575\,\text{mol}}\right) = 0.261\,\text{L} = 261\,\text{mL}$$

Or using $M_1V_1 = M_2V_2$:

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(3.00\,\text{M})(0.05000\,\text{L}))}{0.575\,\text{M}} = 0.261\,\text{L}$$

Exercise 1.7.9

1. Find moles of CaCl_2:

$$0.250\,\frac{\text{mol}}{\text{L}} \times 0.0200\,\text{L} = 0.00500\,\text{mol CaCl}_2$$

2. Use mole ratio to find moles of Na_3PO_4 needed:

$$0.00500\,\text{mol CaCl}_2 \times \frac{2\,\text{mol Na}_3\text{PO}_4}{3\,\text{mol CaCl}_2} = 0.00333\,\text{mol Na}_3\text{PO}_4$$

3. Find volume of Na_3PO_4 needed:

$$\frac{0.00333\,\text{mol}}{0.300\,\frac{\text{mol}}{\text{L}}} = 0.0111\,\text{L} = 11.1\,\text{mL}$$

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1.8: Useful Math Functions in Chemistry

Learning Objective

- Become familiar with the mathematical concepts and calculator functions used throughout this course, including scientific notation, fractions, order of operations (BEDMAS), exponents, logarithms, the quadratic equation, rearranging equations, and interpreting graphs.

Chemistry uses mathematics to describe and predict the behaviour of matter. Throughout this course, you will perform calculations involving quantities such as measurements, concentrations, energies, and reaction rates. This section reviews the mathematical concepts and calculator functions used most often in first-year chemistry. Becoming comfortable with these skills now will help you focus on the chemistry later.

Scientific Notation

Scientists often work with very large or small numbers. For example, a commonly-used approximation of Avogadro's number (which represents the number of atoms or molecules in 1 mole) written out would be 602 200 000 000 000 000 000 000 000. Writing and working with numbers in this form is not practical.

Instead, scientists use a system called scientific notation to show these numbers. In scientific notation, numbers are written using the form $c \times 10^n$, where:

- c is a coefficient, which is a number usually between 1 and 10
  - (Note: In CHM 135H, you may possibly encounter some numbers that have a coefficient less than 1 or larger than 10)
- n is an integer (a whole number that is either positive, negative, or 0)

The exponential term 10^n is called a power of 10. Powers of 10 can make numbers bigger or smaller by changing the position of the decimal place. Consider a few examples below:

Power of 10	Value
10^3	1000
10^2	100
10^1	10
10^0	1
10^{-1}	0.1
10^{-2}	0.01
10^{-3}	0.001

Each time the exponent (n value) increases by 1, the value becomes 10 times bigger. Also, each time the exponent decreases by 1, the value becomes 10 times smaller.

- We can see that multiplying a number by 10 shifts every digit 1 decimal place to the right (thus making the number 10 times larger), and multiplying by 100 or 1000 shifts every digit 2 or 3 decimal places to the right, respectively.
- Conversely, multiplying a number by 0.1 shifts every digit 1 decimal place to the left (thus making the number 10 times smaller), and multiplying by 0.01 or 0.001 shifts every digit 2 or 3 decimal places to the left, respectively.

Therefore, the exponent in 10^n indicates how many places the original decimal point moves, and whether it is to the right or left:

- If n is positive, then the decimal place is moved n times to the right, making the number 10^n times larger.
- If n is negative, then the decimal place is moved n times to the left, making the number 10^n times smaller.
- If n is 0, then the number of interest equals the coefficient. This is because $10^0 = 1$, and multiplying any coefficient by 1 does not change its value.

In terms of Avogadro's number, it is much more convenient to write it in scientific notation, as 6.022×10^{23}. In this form, Avogadro's number becomes easier to both write out by hand, and also easier to insert in a calculator.

Exercise 1.8.1

Faraday's constant, F, represents the total electrical charge per 1 mole of electrons, and is measured in units of coulombs per mole (C/mol). The value of F is approximately 96490 C/mol. What is F, expressed in scientific notation?

Answer available at the end of this section.

Exercise 1.8.2

The acid dissociation constant (K_a) of acetic acid, $\mathrm{CH_3COOH}$, is 0.0000175 and is unitless. What is the K_a of acetic acid, in scientific notation?

Answer available at the end of this section.

Using Scientific Notation in a Calculator

Scientific calculators have a dedicated **exponent button** that allows numbers in scientific notation to be entered as a single value, rather than typing the coefficient and multiplying by 10^n separately. Depending on the calculator model, this button may be labeled one of the following:



Using the exponent button saves time and helps prevent typing mistakes. More importantly, the calculator treats the entire expression $c \times 10^n$ as a single number, avoiding potential order-of-operation errors that can occur when 10^n is entered as a separate multiplication.

Exercise 1.8.3

Using your scientific calculator, evaluate the following. Make sure to round to the correct number of significant figures.

a) $(3.2 \times 10^3) + (4.8 \times 10^2)$

b) $(5.4 \times 10^{-2}) - (4.0 \times 10^{-3})$

c) $(2.35 \times 10^{-3}) \times (4.00 \times 10^5)$

d) $(8.4 \times 10^{-2}) \div (2.1 \times 10^{-5})$

e) $(1.30 \times 10^{-2})^2$

f) $(1.20 \times 10^{-2})^3$

g) $\sqrt{4.9 \times 10^{-5}}$

Answer available at the end of this section.

Fractions

A fraction represents a ratio between two values.

Many quantities in chemistry are expressed as fractions or ratios. For example, density is the ratio of mass to volume, molarity is the ratio of the number of moles of solute to the volume of the solution, and the mole fraction is the fraction of the total number of particles that are of a specific substance. Similarly, the coefficients in a balanced chemical equation represent mole ratios, which describe the relative amounts of reactants and products. These mole ratios act as conversion factors and are the foundation of stoichiometry, allowing us to calculate the amount of one substance produced or consumed from a known amount of another substance.

Exercise 1.8.4

Silver oxide decomposes according to the balanced chemical equation:

$\mathrm{Ag_2O(s)} \rightarrow 2\mathrm{Ag(s)} + \frac{1}{2}\mathrm{O_2(g)}$.

The balanced equation shows that 1 mole of silver oxide produces 2 moles of silver and 0.5 moles of oxygen gas. If 4.0 moles of $\mathrm{Ag_2O(s)}$ decompose completely, how many moles of silver and oxygen gas will be produced?

Answer available at the end of this section.

Multiplying and Dividing Fractions

To multiply fractions, multiply the numerators together and multiply the denominators together.

To divide fractions, multiply by the reciprocal of the second fraction.

Exercise 1.8.5

Solve the following: $\frac{1}{3} \times \frac{4}{2}$

Answer available at the end of this section.

Exercise 1.8.6

Solve the following: $\frac{5}{2} \div \frac{4}{3}$

Answer available at the end of this section.

Order of Operations

Many chemistry equations and calculations rely on a wide range of mathematical operations such as addition, subtraction, multiplication, division, exponentials, and logarithms. For example, consider the Henderson-Hasselbalch equation, $pH = pK_a + log(\frac{[A^-]}{[HA]})$, which is used to find the pH of a buffer solution. To solve this equation for pH, you would need to know which order to calculate the brackets, logarithms, division, and addition.

The order of operations followed in mathematics is known by an acronym called **BEDMAS**, which stands for:

Brackets

Exponents (and Logarithms)

Division

Multiplication

Addition

Subtraction

When doing calculations, each calculation must be performed reading from **left to right** in the order presented by BEDMAS. Therefore, you first perform bracket operations (with BEDMAS rules still applying inside the brackets), then perform non-bracket operations in the order of exponents and logarithms, division, multiplication, addition, then subtraction.

If an equation or calculation does not contain one or more of the BEDMAS operations, the operations that come after them are considered next.

Exercise 1.8.7

What is $(32 + 71 \div 10) + (9^2 + 8.4)$?

Answer available at the end of this section.

Exercise 1.8.8

What is $(2.0 \times 4.1)^2 + (3—1)^3$?

Answer available at the end of this section.

Exercise 1.8.9

A buffer has a weak acid concentration, $[\mathrm{HA}]$, of 0.060 M and a conjugate base concentration, $[\mathrm{A}^-]$, of 36 M. Given the pK_a is 4.00, use the Henderson-Hasselbalch equation, $pH = pK_a + log(\frac{[A^-]}{[HA]})$, to find the pH of the solution.

Answer available at the end of this section.

Exponents and Logarithms

In chemistry, many relationships involve quantities that change exponentially rather than linearly. As a result, exponents and logarithms are used to describe phenomena such as radioactive decay, reaction rates, acid-base chemistry (through pH and pOH), and chemical equilibrium.

In mathematics, an **exponential** expression is made up of a number called a **base** that is raised to an **exponent (or power).** An exponent indicates that a base is multiplied by itself repeatedly. Exponential expressions are of the form $b^x = y$, where:

- b is the base
- x is the exponent
- y is the value

Some examples of common bases are 10 and Euler's number, $e \approx 2.71828$. The exponent can either be positive or negative.

Exercise 1.8.10

Show how the following exponentials can be written as a product using their bases. Then, evaluate.

a) 4^3

b) 10^4

Answer available at the end of this section.

A **logarithm** is the **inverse** of an exponential expression. It is written as $log_b(y) = x$, where:

- b is the base
- x is the exponent
- y is the value (also sometimes called the argument)

While an exponential expression ($b^x = y$) tells us the value obtained by raising a base to an exponent, a logarithm ($log_b(y) = x$) tells us the exponent to which the base must be raised to obtain a given value.

The inverse relationship between exponents and logarithms can be stated as: $b^x = y \Leftrightarrow log_b(y) = x$

Common Logarithm and Natural Logarithm

Two unique logarithms are used frequently in chemistry:

- **Common logarithm (base 10):** The common logarithm has a base of 10 and is written as $\log_{10}(y) = x$. In practice, the base is almost always omitted, so it is written as $\log(y) = x$.
- **Natural logarithm (base e):** The natural logarithm has a base of $e \approx 2.71828$. Instead of writing $\log_e(y) = x$, the notation $\ln(y) = x$ is used.

Most scientific calculators have separate **log** and **ln** buttons. The **log** button calculates the common logarithm (base 10), while the **ln** button calculates the natural logarithm (base e).

Exercise 1.8.11

Evaluate the following, and convert from logarithmic form to exponential form.

a) $log(100)$

b) $ln(62)$

Answer available at the end of this section.

Laws of Exponents

The laws of exponents are algebraic rules that help simplify mathematical expressions involving powers with a common base, b:

Name of Exponent Law	Rule	Description
Product Rule	$b^m b^n = b^{m+n}$	When multiplying two expressions, their exponents are added together.
Quotient Rule	$\frac{b^m}{b^n} = b^{m-n}$	When dividing two expressions, the denominator's exponent is subtracted from the numerator's exponent.

Negative Exponent	$b^{-m} = \frac{1}{b^m}$	Any base raised to a negative exponent equals the reciprocal of that expression.
Zero Exponent	$b^0 = 1$, where $b \neq 0$	Any non-zero number raised to the power of 0 equals 1.
Power of a Power	$(b^m)^n = b^{mn}$	When an expression with a power is raised to another power, the exponents are multiplied together.
Power of a Product	$(ab)^m = a^m b^m$	When a product is raised to a power, each factor is raised to that same power.
Power of a Quotient	$(\frac{a}{b})^m = \frac{a^m}{b^m}$	When a quotient is raised to a power, each factor is raised to that same power.

Laws of Logarithms

The laws of logarithms are closely tied to the laws of exponents, and they help simplify expressions involving logarithms. The laws of logarithms apply to any valid base, including the common logarithm $(\log)$ and natural logarithm $(\ln)$ used frequently in chemistry.

Name of Logarithm Law	Rule	Description
Product Rule	$log_b(MN) = log_b(M) + log_b(N)$	The logarithm of a product is the sum of the logarithms (addition).
Quotient Rule	$log_b(\frac{M}{N}) = log_b(M) - log_b(N)$	The logarithm of a quotient is the difference of the logarithms (subtraction).
Power Rule	$log_b(M^N) = Nlog_b(M)$	The exponent inside a logarithm can be moved to the front as a coefficient.
Zero Rule	$log_b(1) = 0$	The logarithm of 1 to any valid base is always equal to 0.
Identity Rule	$log_b(b) = 1$	The logarithm of a base to itself is always equal to 1.

Exercise 1.8.12

Evaluate the following on your scientific calculator.

a) $(2^3 - 3^{-4})^2$

b) $ln(e^5) + ln(24)$

c) $log(\frac{23}{10})$

Answer available at the end of this section.

Exercise 1.8.13

In chemistry, the rate of a reaction can be modelled using the Arrhenius equation, $k = Ae^{-E_a/RT}$, where:

- k is the rate constant (in s^{-1})
- A is the frequency factor (in s^{-1})
- E_a is the activation energy (in J/mol)
- R is the universal gas constant (8.314 J mol^{-1} K^{-1})
- T is the temperature (in K)

We will explore this further in Chapter 6 (Chemical Kinetics). For now, let's look at the calculations using exponents and logs.

a) If $A = 1.0 \times 10^6$ s^{-1}, $E_a = 7500$ J/mol, and $T = 650$ K, calculate the rate constant, k.
b) If $A = 1.2 \times 10^{10}$ s^{-1}, $k = 4.1 \times 10^6$ s^{-1}, and $T = 720$ K, calculate the activation energy, E_a.

Answer available at the end of this section.

Rearranging Equations

Many chemistry problems require rearranging equations to isolate an unknown variable. Developing this skill makes it easier to solve equations involving concentrations, gas laws, equilibrium, kinetics, and many other quantitative relationships. The following examples illustrate common algebraic techniques, including solving linear equations, systems of equations, and logarithmic equations. Although the examples use specific numerical values, the same algebraic steps apply to any equation of the same form.

The key to rearranging equations is that whatever operation you perform on one side of the equation, you must perform the same operation on the other side to maintain equality. For example, if you add or subtract the same quantity from both sides, the two sides remain equal. The same is true if you multiply or divide both sides by the same nonzero quantity. Repeating these steps allows you to isolate the unknown variable.

Exercise 1.8.14

Solve for y if $5 = \frac{y}{4} - 3$

Answer available at the end of this section.

Exercise 1.8.15

Solve for x if $(8)(48 - x)(3.5) = (2.5)(x - 12)(0.2)$

Answer available at the end of this section.

Exercise 1.8.16

Solve for y if $\ln\left(\frac{y}{0.40}\right) = -2.0 \times 10^{-2}(1.5)$

Answer available at the end of this section.

Exercise 1.8.17

Solve for x if $10^{-x} = 3.2$

Answer available at the end of this section.

Exercise 1.8.18

Solve the system of equations:

$2x + y = 24$

$x - y = 8$

Answer available at the end of this section.

Exercise 1.8.19

Solve the system of equations:

$x + y = 12$

$\frac{x}{50} + 2\left(\frac{y}{200}\right) = 0.18$

Answer available at the end of this section.

The Quadratic Equation

A quadratic equation is an equation in which the highest exponent of x is 2. In chemistry, quadratic equations often appear in calculations involving chemical equilibria.

Standard Form of a Quadratic Equation

$ax^2 + bx + c = 0$

where:
- a is the coefficient of x^2
- b is the coefficient of x
- c is the constant term

The solutions of a quadratic equation are the values of x that make the equation equal to zero, given specific values of a, b, and c.

The Quadratic Formula

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

The ± symbol indicates that there are two possible solutions for x, one obtained by addition and one by subtraction.

Exercise 1.8.20

Solve for x if $5x^2 - 9x - 2 = 0$.

Answer available at the end of this section.

Exercise 1.8.21

Solve for x if $-10 = 11x - 6x^2$

Answer available at the end of this section.

Interpreting Graphs

Graphs are an important tool in chemistry because they allow relationships between variables to be visualized and analyzed. In many experiments, one variable is controlled by the experimenter and is called the **independent variable**, while the other changes in response and is called the **dependent variable**.

Graphs are an important tool for visualizing relationships between variables and interpreting experimental data in chemistry. The **independent variable** is typically plotted on the **x-axis**, while the **dependent variable** is plotted on the **y-axis**, giving the general form **y=f(x)**. Several types of relationships commonly occur in chemistry, such as **linear**, **inverse**, and **exponential** relationships, illustrated in **Figure 1**.

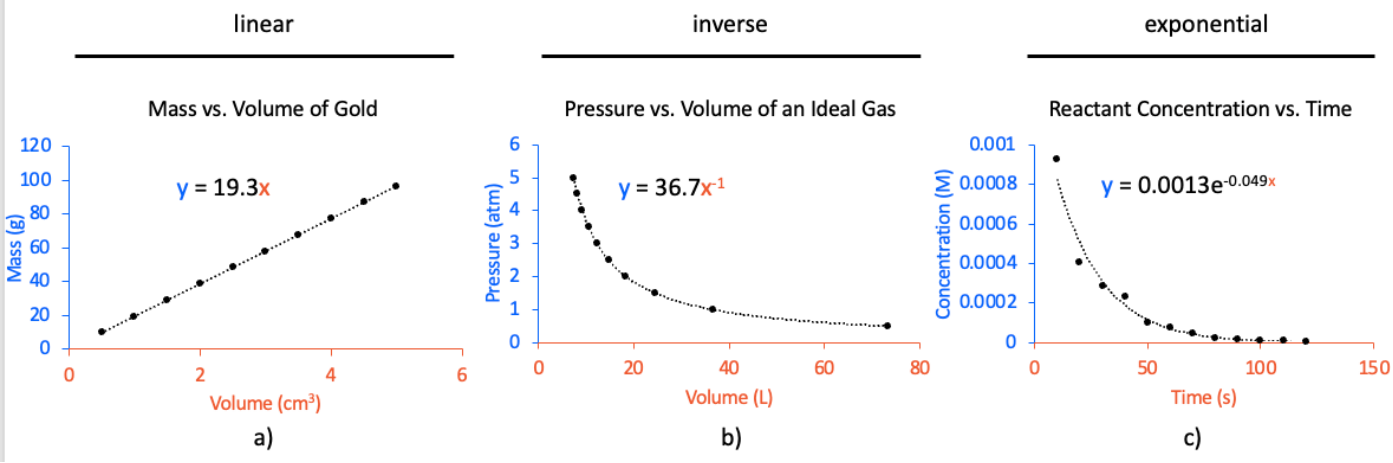


Figure 1.8.1**.** Common graphical relationships encountered in chemistry. **(a)** A linear relationship, illustrated by mass versus volume for copper, where mass increases at a constant rate with volume because the density remains constant. **(b)** An inverse relationship, illustrated by pressure versus volume for an ideal gas, where pressure decreases as volume increases. **(c)** An exponential relationship, illustrated by reactant concentration versus time, where the concentration of the reactant decreases exponentially during reaction.

Linear Relationships

A linear relationship exists when two variables change at a constant rate. A straight line can be represented by the equation $y = mx + b$, where

- m is the slope of the line.
- b is the y-intercept, the value of y at the x-axis (i.e. when $x = 0$)

The slope describes how much the dependent variable (y) changes for every unit increase in the independent variable (x). The vertical distance is called the **rise** and the horizontal distance is called the **run**, as shown in Figure 1.8.2.

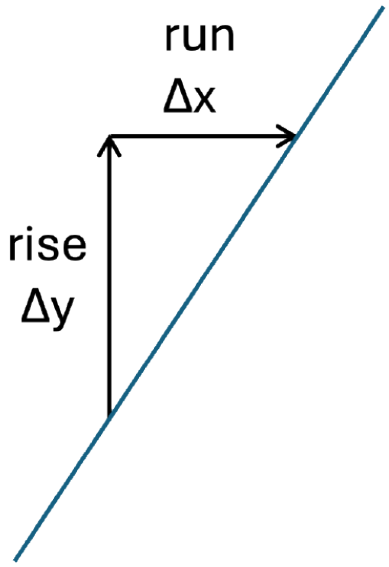


Figure 1.8.2**.** Slope of a line

The slope of a straight line is calculated using $m = \frac{rise}{run} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$

where

- Δy is the change in the vertical direction, the rise.
- Δx is the change in the horizontal direction, the run.

The **slope** (m) of a straight line represents the rate at which the **dependent variable** changes with respect to the **independent variable**.

- A **positive slope** $(m > 0)$ indicates that the dependent variable increases as the independent variable increases.
- A **negative slope** $(m < 0)$ indicates that the dependent variable decreases as the independent variable increases.

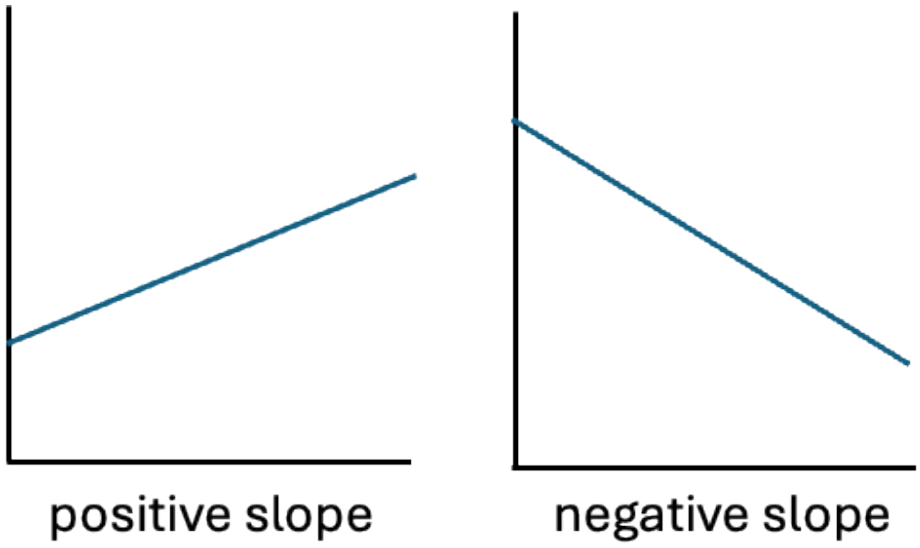
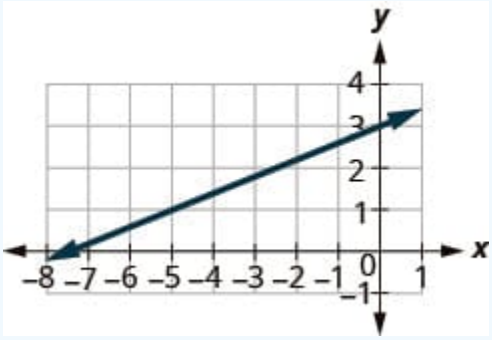


Figure 1.8.3**.** A positive slope indicates that the dependent variable increases with the independent variable (i.e. the line is "up hill"). A negative slope indicates that the dependent variable decreases as the independent variable increases (i.e. the line is "down hill.")

Exercise 1.8.22

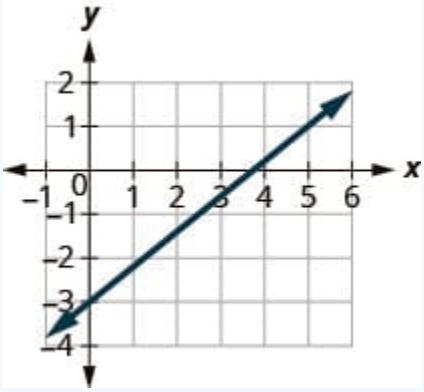
What is the equation of the line shown in the plot below?



Answer available at the end of this section.

Exercise 1.8.23

What is the equation of the line shown in the plot below?



Answer available at the end of this section.

Answers

Exercise 1.8.1

First, we must identify the coefficient. In Faraday's constant, the coefficient is 9.649.

Next, we must move the decimal place to the right or left of the coefficient to identify the exponent (n value). Here, we move the decimal place 4 times to the right from 9.649, in order to attain the original value of 96490.

Thus, Faraday's constant expressed in scientific notation would be 9.649×10^4 C/mol. **Always remember to include units, if provided.**

Exercise 1.8.2

First, we must identify the coefficient. For the K_a of acetic acid, the coefficient is 1.75.

Next, we must move the decimal places to the right or left of the coefficient to identify the exponent (n value). Here, we move the decimal place 5 times to the left from 1.75, in order to attain the original value of 0.0000175.

Thus, the K_a of acetic acid expressed in scientific notation would be 1.75×10^{-5}. **Since K_a is unitless, there are no units in the final answer.**

Exercise 1.8.3

a) 3.7×10^3

b) 5.0×10^{-2}

c) 9.40×10^2

d) 4.0×10^3

e) 1.69×10^{-4}

f) 1.73×10^{-6}

g) 7.0×10^{-3}

Exercise 1.8.4

Using the mole ratios from the balanced equation:

$\mathrm{Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2}O_2(g)}$

Moles of silver (Ag):

$$4.0 \text{ mol } \mathrm{Ag_2O}\left(\frac{2 \text{ mol Ag}}{1 \text{ mol } \mathrm{Ag_2O}}\right) = 4.0 \ \cancel{\text{mol } \mathrm{Ag_2O}}\left(\frac{2 \text{ mol Ag}}{1 \ \cancel{\text{mol } \mathrm{Ag_2O}}}\right) = 8.0 \text{ mol Ag}$$

Moles of oxygen gas (O_2):

$$4.0 \text{ mol } \mathrm{Ag_2O}\left(\frac{0.5 \text{ mol } \mathrm{O_2}}{1 \text{ mol } \mathrm{Ag_2O}}\right) = 4.0 \ \cancel{\text{mol } \mathrm{Ag_2O}}\left(\frac{0.5 \text{ mol } \mathrm{O_2}}{1 \ \cancel{\text{mol } \mathrm{Ag_2O}}}\right) = 2.0 \text{ mol } \mathrm{O_2}$$

Exercise 1.8.5

$\frac{1\times4}{3\times2} = \frac{4}{6} = \frac{2}{3} = 0.667$

Exercise 1.8.6

Step 1: Rewrite the division as multiplication by the reciprocal

$\frac{5}{2} \div \frac{4}{3} = \frac{5}{2} \times \frac{3}{4}$

Step 2: Multiply the numerators and denominators

$\frac{5\times3}{2\times4} = \frac{15}{8}$

Step 3: Simplify the fraction

$\frac{15}{8} = 1.875$

Exercise 1.8.7

Step 1: Identify all the operations present in the calculation, and list them in the correct order according to BEDMAS.

In this problem, there are brackets, exponents, division, and addition.

Step 2: Solve the problem following the correct BEDMAS order.

$(32 + 71 \div 10) + (9^2 + 8.4)$

$= (32 + 71 \div 10) + (81 + 8.4)$

$= (32 + 7.1) + (81 + 8.4)$

$= 39.1 + 89.4$

$= 128.5$

Exercise 1.8.8

Step 1: Identify all the operations present in the calculation, and list them in the correct order according to BEDMAS.

In this problem, there are brackets, exponents, multiplication, addition, and subtraction.

Step 2: Solve the problem following the correct BEDMAS order.

$(2.0 \times 4.1)^2 + (3—1)^3$

$= (8.2)^2 + (2)^3$

$= 67.24 + 8$

$= 75.24$

Exercise 1.8.9

Step 1: Identify all the operations present in the calculation, and list them in the correct order according to BEDMAS.

In the Henderson-Hasselbalch equation, there is a logarithm, division, and addition.

Step 2: Solve the problem following the correct BEDMAS order.

$pH = pK_a + log(\frac{[A^-]}{[HA]})$

$pH = 4.00 + log(\frac{36M}{0.06M})$

Then, the units of M cancel from the numerator and denominator:

$pH = 4.00 + log(\frac{36}{0.06})$

$pH = 4.00 + log(600)$

$pH \approx 4.00 + 2.7782$

$pH \approx 6.7782$

$pH \approx 6.78$

Thus, the pH of the solution is approximately 6.78.

Exercise 1.8.10

a) The base is 4 and the exponent is 3.

4^3 can be expressed as $4 \times 4 \times 4 = 64$.

Thus, $4^3 = 64$.

b) The base is 10 and the exponent is 4.

10^4 can be expressed as $10 \times 10 \times 10 \times 10 = 10000$.

Thus, $10^4 = 10000$.

Exercise 1.8.11

a) To attain a value of 100, 10 must be raised to an exponent of 2.

Therefore, $log(100) = 2 \Leftrightarrow 100 = 10^2$.

b) To attain a value of 62, e must be raised to an exponent of approximately 4.13.

Therefore, $ln(62) \approx 4.13 \Leftrightarrow 62 \approx e^{4.13}$.

Exercise 1.8.12

a) 63.8

b) 8.18

c) 0.362

Exercise 1.8.13

a) ***Hint:*** *In this problem, the units in the exponent cancel, so they have been omitted from the calculations to focus on mathematical operations. However, for chemistry problems in CHM 135H, it is highly recommended that you include all units and explicitly show how they cancel, if applicable.*

Substitute the known values:

$$k = Ae^{-E_a/RT}$$

$$k = (1.0 \times 10^6\ s^{-1})(e^{-7500/(8.314)(650)})$$

$$k = (10^6\ s^{-1})(e^{-7500/5404.1})$$

$$k \approx (10^6\ s^{-1})(e^{-1.388})$$

$$k \approx 2.5 \times 10^5\ s^{-1}$$

b) To solve for E_a, start with the Arrhenius equation. Begin by taking the natural logarithm of both sides. Since the natural logarithm is the inverse of the exponential function, applying $\ln$ eliminates the exponential:

$$k = Ae^{-E_a/RT}$$

$$\ln(k) = \ln\left(Ae^{-E_a/RT}\right)$$

Use the product rule for logarithms, $\ln(MN) = \ln(M) + \ln(N)$:

$$\ln(k) = \ln(A) + \ln\left(e^{-E_a/RT}\right)$$

Since $\ln(e^x) = x$,

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

Rearrange to isolate E_a:

$$E_a = RT\left[\ln(A) - \ln(k)\right]$$

Substitute the known values:

$$E_a = (8.314\ \text{J mol}^{-1}\,\text{K}^{-1})(720\ \text{K})\left[\ln(1.2 \times 10^{10}) - \ln(4.1 \times 10^{6})\right]$$

The units of K cancel, leaving J and mol^{-1} (recall that units raised to -1 become reciprocals, so $J\ \ mol^{-1}$ is J/mol).

$$E_a \approx (8.314\ \text{J/mol})(720)(23.21 - 15.23)$$

$$E_a \approx 4.8 \times 10^4\ \text{J/mol}$$

Exercise 1.8.14

Step 1: Eliminate the constant term

The variable y is divided by 4, but before dealing with the division, remove the -3 by adding 3 to both sides of the equation:

$5 + 3 = \frac{y}{4} - 3 + 3$

$8 = \frac{y}{4}$

Step 2: Eliminate the division by 4

Multiply both sides of the equation by 4 to isolate y:

$8(4) = \frac{y}{4}(4)$

$32 = y$

$y = 32$

Exercise 1.8.15

Step 1: Simplify each side by multiplying the constants:

$28(48 - x) = 0.5(x - 12)$

Step 2: Expand both sides of the equation:

$1344 - 28x = 0.5x - 6$

Step 3: Move all x-terms to one side of the equation:

$1344 - 28x + 28x = 0.5x + 28x - 6$

$1344 = 28.5x - 6$

Step 4: Move the constant term to the other side:

$1344 + 6 = 28.5x - 6 + 6$

$1350 = 28.5x$

Step 5: Isolate x:

$\frac{1350}{28.5} = \frac{28.5}{28.5}x$

$x = \frac{1350}{28.5}$

$x \approx 47.4$

Exercise 1.8.16

Step 1: Simplify the right side of the equation

$\ln\left(\frac{y}{0.40}\right) = -0.030$

Step 2: Eliminate the natural logarithm

Natural logarithms and exponential functions are inverse operations. Just as addition is undone by subtraction and multiplication is undone by division, a natural logarithm is undone by raising e to the same power:

$ln(y) = x \quad \iff \quad y = e^x$

Raise both sides of the equation as powers of e. Because the natural logarithm and the exponential function are inverse operations, $e^{ln(x)} = x$.

Applying this to both sides:

$e^{ln(\frac{y}{0.40})} = e^{-0.030}$

$\frac{y}{0.40} = e^{-0.030}$

Step 3: Evaluate the exponential

$\frac{y}{0.40} = 0.970$

Step 4: Isolate y

Multiply both sides by 0.40.

$y = 0.388$

Exercise 1.8.17

The common logarithm (log) and powers of 10 are inverse operations.

$log(y) = x \quad \iff \quad y = 10^x$

Step 1: Eliminate the exponential

Take the base-10 logarithm of both sides.

$\log(10^{-x}) = \log(3.2)$

Step 2: Evaluate the logarithm

$-x = \log(3.2)$

$-x = 0.505$

Step 3: Isolate x

Multiply both sides by –1.

$x = -0.505$

Exercise 1.8.18

Step 1: Add the two equations to eliminate y

We add the left-hand sides and right-hand sides of the equations. Since $+y$ and $-y$ cancel, the variable y is eliminated, allowing us to solve for x:

$(2x + y + +(x - y) = 24 + 8$

$3x = 32$

Step 2: Solve for x

$x = \frac{32}{3} = 10.67$

Step 3: Substitute back to find y

Substitute $x = 10.67$ into one of the original equations: Using $x - y = 8$:

$10.67 - y = 8$

$y = 2.67$

Exercise 1.8.19

In this case, adding the equations will not eliminate either variable. Instead, we use substitution, which is often useful when one equation can be easily rearranged to isolate a variable.

Step 1: Rearrange the first equation to isolate one variable

$x = 12 - y$

Step 2: Substitute into the second equation

Replace x with $12 - y$:

$\frac{12-y}{50} + 2\left(\frac{y}{200}\right) = 0.18$

Step 3: Simplify each term

$\frac{12}{50} - \frac{y}{50} + \frac{2y}{200} = 0.18$

$0.24 - 0.02y + 0.01y = 0.18$

Step 4: Solve for y

Combine like terms:

$0.24 - 0.01y = 0.18$

$-0.01y = -0.06$

$y = 6$

Step 5: Substitute back to find x

$x = 12 - 6 = 6$

Exercise 1.8.20

Step 1: Identify coefficients

$a = 5, \qquad b = -9, \qquad c = -2$

Step 2: Substitute into the quadratic formula

$x = \frac{-(-9) \pm \sqrt{(-9)^2 - 4(5)(-2)}}{2(5)}$

Step 3: Simplify the discriminant

It is often helpful to simplify the expression under the square root first. Breaking the calculation into smaller steps reduces errors and makes it easier to evaluate the discriminant ($b^2 - 4ac$), which determines the values of x.

$(-9)^2 = 81$

$4(5)(-2) = -40$

$81 - (-40) = 121$

$\sqrt{121} = 11$

$x = \frac{9 \pm 11}{10}$

Step 4: Find both solutions

$x = \frac{9+11}{10} = \frac{20}{10} = 2$

$x = \frac{9-11}{10} = \frac{-2}{10} = -0.2$

Choosing the Correct Solution

The mathematical solutions are x = 2 and x = –0.2. In chemistry applications, negative values for quantities such as concentration, pressures, or amounts are often not physically meaningful. In these cases, the only physically valid solution is used.

Exercise 1.8.21

Step 1: Rewrite in standard form

Add 10 to both sides and arrange in descending powers of x:

$6x^2 - 11x - 10 = 0$

Step 2: Identify the coefficients

$a = 6, \qquad b = -11, \qquad c = -10$

Step 3: Substitute into the quadratic formula

$x = \frac{-(-11) \pm \sqrt{(-11)^2 - 4(6)(-10)}}{2(6)}$

Step 4: Simplify the discriminant

Simplify the expression inside the quadratic formula **before calculating the final solutions**. Breaking the calculation into smaller steps reduces errors and makes it easier to evaluate the discriminant ($b^2 - 4ac$), which determines the values of x.

$(-11)^2 = 121$

$4(6)(-10) = -240$

$121 - (-240) = 361$

$\sqrt{361} = 19$

$x = \frac{11 \pm 19}{12}$

Step 5: Find both solutions

$x = \frac{11+19}{12} = \frac{30}{12} = 2.5$

$x = \frac{11-19}{12} = \frac{-8}{12} = -0.667$

Choosing the Correct Solution

The mathematical solutions are x = 2.5 and x = –0.667. In chemistry contexts, negative values for quantities such as concentrations, pressures, or amounts are not physically meaningful. In such cases, the valid solution is x = 2.5

Exercise 1.8.22

To find the equation of the line, we need the form $y = mx + b$

Step 1: Identify two points on the line with clearly defined coordinates.

Let's choose the points (0,3) and (-7,0).

Step 2: Find the rise and run between the two points.

The rise is $\Delta y = 3 - 0 = 3$.

The run is $\Delta x = 0 - (-7) = 7$.

Step 3: Calculate the slope

$m = \frac{\text{rise}}{\text{run}}$

$m = \frac{3}{7}$

Step 4: Substitute the slope and the y-intercept into the equation.

Since the line crosses the y-axis at (0,3), b=3.

Substituting the y-intercept and slope into $y = mx + b$ gives the equation of the line $y = \frac{3}{7}x + 3$.

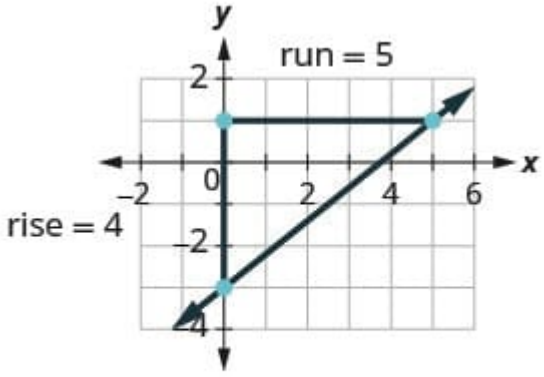
Exercise 1.8.23

To find the equation of the line, we need the form $y = mx + b$

Step 1: Identify two points on the line with clearly defined coordinates

Let's use (0,-3) and (5,1).

Step 2: Calculate the slope using the rise and run between the two points:



The rise is 4.

The run is 5.

$m = \frac{\text{rise}}{\text{run}}$

$m = \frac{1-(-3)}{5-0}$

$m = \frac{4}{5}$

Step 3: Substitute the slope and the y-intercept into the equation:

Since the line crosses the y-axis at (0,-3), b=-3. $y = \frac{4}{5}x - 3$

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1.E: Foundations for Success (Exercises)

Units and Measurements

Exercise $1.E.1$

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 two units. How many significant figures can you justify in your conversion factor?

Answer available at the end of this section.

Exercise $1.E.2$

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. What is the density of the jewelry?

Answer available at the end of this section.

Exercise $1.E.3$

A chemist needs to measure out 0.214 mL of benzene but doesn't have equipment precise enough to measure such a small volume. However, they do have an analytical balance that can measure to ± 0.0001 g. If the density of benzene is 0.8765 g/mL, how many grams of benzene should the chemist weigh out?

Answer available at the end of this section.

Exercise $1.E.4$

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

(a) 628×342

(b) $\left(5.63 \times 10^2\right) \times \left(7.4 \times 10^3\right)$

(c) $\dfrac{28.0}{13.483}$

(d) 8119×0.000023

(e) $14.98 + 27340 + 84.7593$

(f) $42.7 + 0.259$

Answer available at the end of this section.

Exercise $1.E.5$

A beetle scurries across a sidewalk at a speed of 4.20 cm/s. What is this speed in kilometres per hour (km/h)?

Answer available at the end of this section.

Exercise 1.E.6

The coronavirus (SARS-CoV-2) is roughly spherical with a 5.2×10^{-4} μm^3.

a) What is this volume in mm^3?

b) What is the total volume occupied by 10^{10} virus particles in litres?

Conversion factors

- 10^6 µm = 1 m
- 1000 mm = 1 m
- 1000 L = 1 m^3

Answer available at the end of this section.

Exercise 1.E.7

A recipe for oatmeal chocolate chip cookies uses 1.5 cups of oats. How many milligrams of calcium does this provide?

From oatmeal packaging:

1 serving = 1/3 cup

1 serving = 20 mg Ca

Answer available at the end of this section.

Atoms, Elements, and the Mole

Exercise 1.E.8

How are electrons and protons similar? How are they different?

Answer available at the end of this section.

Exercise 1.E.9

Iodine-131 ($^{131}\mathrm{I}$) is a radioactive isotope commonly used to treat thyroid conditions. How many protons, neutrons, and electrons are in a neutral atom of iodine-131?

Answer available at the end of this section.

Exercise 1.E.10

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

Answer available at the end of this section.

Exercise 1.E.11

What is the mass of 0.250 mol of magnesium (Mg)?

Answer available at the end of this section.

Exercise 1.E.12

How many moles are in 14.0 g of silicon (Si)?

Answer available at the end of this section.

Exercise 1.E.13

How many gold atoms are there in a 0.35 g sample of gold (Au)?

Answer available at the end of this section.

Exercise 1.E.14

What is the mass of 2.31 x 10^{21} atoms of aluminum (Al)?

Answer available at the end of this section.

Compounds

Exercise 1.E.15

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

Answer available at the end of this section.

Exercise 1.E.16

For each of the following pairs of ions, write the formula of the compound they will form:

a. $\mathrm{Ca^{2+}}$, $\mathrm{S^{2-}}$
b. $\mathrm{Al^{3+}}$, $\mathrm{Br^{-}}$
c. $\mathrm{Na^{+}}$, $\mathrm{O^{2-}}$

Answer available at the end of this section.

Exercise $1.E.17$

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



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

Answer available at the end of this section.

Exercise $1.E.18$

Why is the symbol for oxygen written as O, but the formula for oxygen gas is written as O_2?

Answer available at the end of this section.

Exercise $1.E.19$

Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

a. Which has the largest number of molecules? Explain why.
b. Which has the greatest mass? Explain why.

Answer available at the end of this section.

Exercise $1.E.20$

The approximate minimum daily dietary requirement of the amino acid leucine, $\mathrm{C_6H_{13}NO_2}$, is 1.1 g. What is this requirement in moles?

Answer available at the end of this section.

Exercise 1.E.21

A woman has approximately 7.5 x 10^{-3} mol of hemoglobin in her blood. The molar mass of hemoglobin is 64456 g/mol.

a) How many hemoglobin molecules does this represent?

b) What is this quantity in grams?

Answer available at the end of this section.

Exercise 1.E.22

Glycine is the simplest amino acid and has the formula $\mathrm{C_2H_5NO_2}$.

a. How many moles are present in 0.125 g of glycine?

b. How many grams of carbon are present in 0.125 g of glycine?

Answer available at the end of this section.

Chemical Reactions and Equations

Exercise 1.E.23

What does it mean for a chemical equation to be balanced, and why does it matter?

Answer available at the end of this section.

Exercise 1.E.24

Balance the following equations:

a. $\mathrm{PCl_5}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{POCl_3}(l) + \mathrm{HCl}(aq)$
b. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow \mathrm{HI}(s)$
c. $\mathrm{Fe}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{Fe_2O_3}(s)$
d. $\mathrm{Na}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{NaOH}(aq) + \mathrm{H_2}(g)$
e. $\mathrm{P_4}(s) + \mathrm{Cl_2}(g) \rightarrow \mathrm{PCl_3}(l)$
f. $\mathrm{PtCl_4}(s) \rightarrow \mathrm{Pt}(s) + \mathrm{Cl_2}(g)$

Answer available at the end of this section.

Reaction Stoichiometry

Exercise 1.E.25

How many moles of water ($\mathrm{H_2O}$) are needed to react completely with 0.35 mol of $\mathrm{TiCl_4}$?

$\mathrm{TiCl_4}(s) + 2\,\mathrm{H_2O}(g) \rightarrow \mathrm{TiO_2}(s) + 4\,\mathrm{HCl}(g)$

Answer available at the end of this section.

Exercise 1.E.26

How many moles of lead metal ($\mathrm{Pb(s)}$) are needed to make 125.2 g of $\mathrm{Pb(OH)_2}$?

$$2\,\mathrm{Pb}(s) + 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow 2\,\mathrm{Pb(OH)_2}(s)$$

Answer available at the end of this section.

Exercise 1.E.27

What mass of $\mathrm{Al_2(SO_4)_3}$ can be made from 13.2 g of Al?

$$2\,\mathrm{Al}(s) + 3\,\mathrm{H_2SO_4}(aq) \rightarrow \mathrm{Al_2(SO_4)_3}(s) + 3\,\mathrm{H_2}(g)$$

Answer available at the end of this section.

Exercise 1.E.28

Silver is often extracted from ores as $\mathrm{K[Ag(CN)_2]}$ and then recovered by the reaction:

$$2\,\mathrm{K[Ag(CN)_2]\,(aq)} + \mathrm{Zn\,(s)} \longrightarrow 2\,\mathrm{Ag\,(s)} + \mathrm{Zn(CN)_2\,(aq)} + 2\,\mathrm{KCN\,(aq)}$$

(a) How many moles of $\mathrm{Zn(CN)_2}$ are produced by the reaction of 35.27 g of $\mathrm{K[Ag(CN)_2]}$?
(b) How many molecules of $\mathrm{Zn(CN)_2}$?
(c) How many grams of $\mathrm{Zn(CN)_2}$?

Answer available at the end of this section.

Exercise 1.E.29

Automotive airbags inflate when a sample of sodium azide, $\mathrm{NaN_3}$, is very rapidly decomposed.

$$2\,\mathrm{NaN_3}(s) \rightarrow 2\,\mathrm{Na}(s) + 3\,\mathrm{N_2}(g)$$

What mass of sodium azide is required to produce 73.6 L of nitrogen gas with a density of 1.25 g/L?

Answer available at the end of this section.

Exercise 1.E.30

0.25 mol of $\mathrm{Al(OH)_3}$ and 0.80 mol HBr are mixed together.

$$\mathrm{Al(OH)_3}(aq) + 3\,\mathrm{HBr}(aq) \rightarrow \mathrm{AlBr_3}(aq) + 3\,\mathrm{H_2O}(l)$$

Which reactant runs out first?

Which reactant is in excess?

Answer available at the end of this section.

Exercise 1.E.31

What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following **unbalanced** equation?

$$\mathrm{Li} + \mathrm{N_2} \rightarrow \mathrm{Li_3N}$$

Answer available at the end of this section.

Exercise 1.E.32

0.50 g of Cr and 0.75 g of $\mathrm{H_3PO_4}$ react according to the following chemical equation?

$$2\,\mathrm{Cr} + 2\,\mathrm{H_3PO_4} \rightarrow 2\,\mathrm{CrPO_4} + 3\,\mathrm{H_2}$$

How many grams of $\mathrm{CrPO_4}$ are produced?

Answer available at the end of this section.

Exercise 1.E.33

A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

$$\mathrm{CaCO_3}(s) \rightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(s)$$

Answer available at the end of this section.

Exercise 1.E.34

Phosphorus pentoxide, $\mathrm{P_4O_{10}}$, is produced by burning phosphorus in oxygen:

$$\mathrm{P_4} + 5\,\mathrm{O_2} \rightarrow \mathrm{P_4O_{10}}$$

a. What is the limiting reactant when 0.200 mol of $\mathrm{P_4}$ and 0.200 mol of $\mathrm{O_2}$ react?
b. Calculate the percent yield if 10.0 g of $\mathrm{P_4O_{10}}$ is collected from the reaction.

Answer available at the end of this section.

Molarity and Solution Stoichiometry

Exercise 1.E.35

Two samples of a salt solution have the same molarity. One sample has a volume of 200 mL, and the other has a volume of 400 mL.

In what ways are the two samples the same?

In what ways are they different?

Answer available at the end of this section.

Exercise 1.E.36

Determine the molarity of 0.000889 g of glycine, $C_2H_5NO_2$, in 1.05 mL of solution.

Answer available at the end of this section.

Exercise 1.E.37

What is the mass of the solute in 0.500 L of 0.30 M glucose, $C_6H_{12}O_6$, used for intravenous injection?

Answer available at the end of this section.

Exercise 1.E.38

What volume of a 1.00 M $Fe(NO_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 M?

Answer available at the end of this section.

Exercise 1.E.39

4.12 L of a 0.850 M H_3PO_4 solution is diluted to a volume of 10.00 L. What is the concentration of the resulting solution?

Answer available at the end of this section.

Exercise 1.E.40

What is the final concentration of the solution produced when 225.5 mL of a 0.09988 M solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

Answer available at the end of this section.

Exercise 1.E.41

What volume of 0.150 M H_2SO_4 is required to completely react with 50.0 mL of 0.100 M $NaOH$ according to the balanced equation:

$$H_2SO_4\,(aq) + 2\,NaOH\,(aq) \rightarrow Na_2SO_4\,(aq) + 2\,H_2O\,(l)$$

Answer available at the end of this section.

Useful Math Functions in Chemistry

Exercise 1.E.42

a) For the following equation, solve for x using the quadratic formula. Round your answers to 2 significant figures:

$$\frac{x^2}{0.75 - x} = 0.60$$

b) Substitute your solutions for x into the original expression to check your calculations (this is a useful strategy for double-checking your work, especially for more-involved calculations).

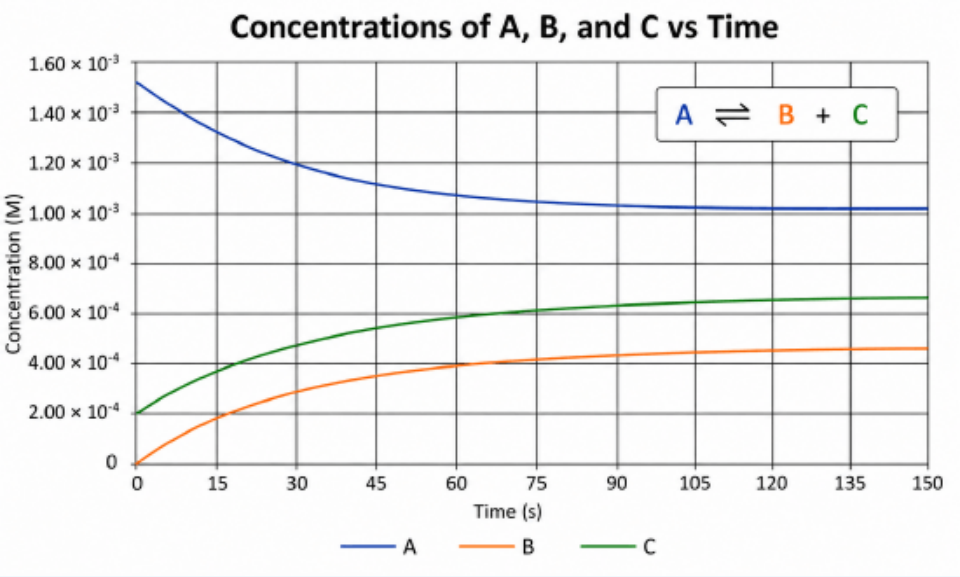
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Exercise $1.E.43$

Below is a graph showing the concentrations of three species (A, B, and C) in a reaction over time.

a) How do the concentrations of each species, $[\mathrm{A}]$, $[\mathrm{B}]$, and $[\mathrm{C}]$, change with time?

b) Is there a linear relationship between $[\mathrm{A}]$ and time?



Answer available at the end of this section.

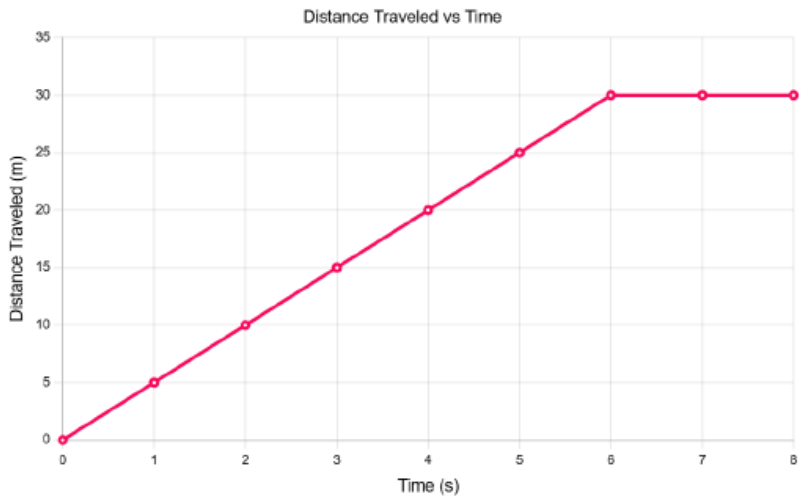
Exercise $1.E.44$

The graph below shows the distance travelled by a particle over time. The average speed of the particle is found by dividing the distance travelled by the time elapsed, using the equation $v = \frac{\Delta d}{\Delta t}$.

a) Is the particle travelling at a constant speed between 0 s and 8 s? Explain your reasoning using the graph.

b) What is the average speed of the particle from 0 s to 6 s? Include the appropriate units.

c) What is the average speed of the particle from 6 s to 8 s? Include the appropriate units.



Answer available at the end of this section.

Exercise $1.E.45$

Consider the equation $y = \sqrt{\frac{3ab}{c}}$:

a) Rearrange the equation to solve for b and c.

b) Calculate y if $a = 3.43 \times 10^4$, $b = 9.20$, and $c = 6.931 \times 10^{-9}$. Write your answer in scientific notation, and round to the correct number of significant figures.

Answer available at the end of this section.

Exercise $1.E.46$

Consider the following equation:

$\ln(u) - \ln(v) = wx$

a) Rearrange the equation to solve for x.

b) Rearrange the equation to solve for u.

c) Calculate x when $u = 0.840$, $v = 0.210$, and $w = 3.50 \times 10^{-2}$. Round your answer to three significant figures.

Answer available at the end of this section.

Exercise $1.E.47$

Consider the following system of equations:

$4m + 3n = 17$

$2m - n = 1$

Solve for m and n.

Answer available at the end of this section.

Additional Problems

Exercise $1.E.48$

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $\mathrm{C_{12}H_{22}O_{11}}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

Answer available at the end of this section.

Exercise $1.E.49$

When aqueous solutions of $\mathrm{BaCl_2}$ and $\mathrm{Na_3PO_4}$ are mixed, the following reaction occurs:

$$3\,\mathrm{BaCl_2\,(aq)} + 2\,\mathrm{Na_3PO_4\,(aq)} \rightarrow \mathrm{Ba_3(PO_4)_2\,(s)} + 6\,\mathrm{NaCl\,(aq)}$$

What mass of $\mathrm{Ba_3(PO_4)_2}$ will precipitate when 45.0 mL of 0.250 M $\mathrm{BaCl_2}$ is mixed with 40.0 mL of 0.200 M $\mathrm{Na_3PO_4}$?

Answer available at the end of this section.

Exercise $1.E.50$

Solid aluminum reacts with aqueous copper(II) sulfate to produce solid copper and aluminum sulfate:

$$2\,\mathrm{Al\,(s)} + 3\,\mathrm{CuSO_4\,(aq)} \longrightarrow 3\,\mathrm{Cu\,(s)} + \mathrm{Al_2(SO_4)_3\,(aq)}$$

If 1.20 g of Al is mixed with 5.00 g of $\mathrm{CuSO_4}$:

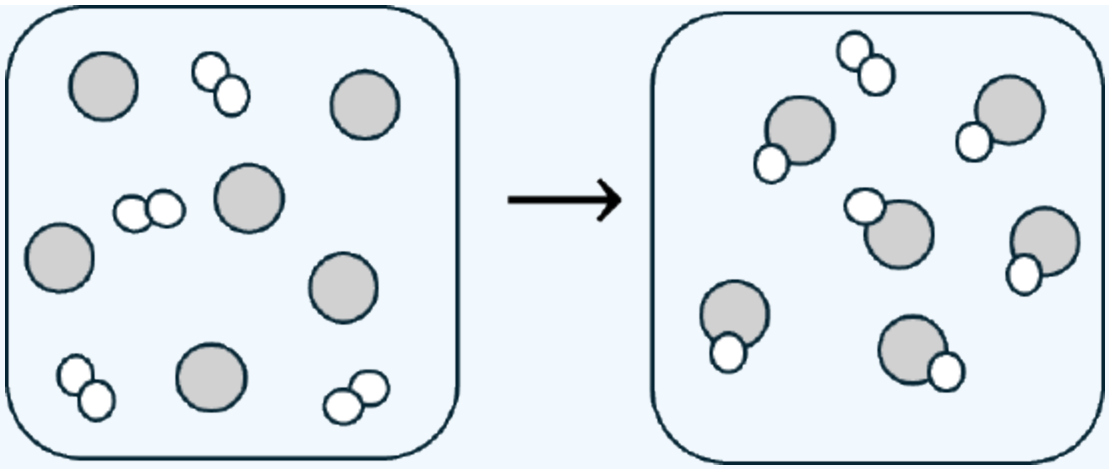
What mass of copper (Cu) is produced?

How much of the excess reactant remains after the reaction?

Answer available at the end of this section.

Exercise $1.E.51$

The following diagram represents the reaction of $\mathrm{A_2\,(g)}$ (joined white spheres) with $\mathrm{B\,(g)}$ (shaded spheres):



a) What is the balanced equation for the reaction? What is the limiting reactant in this diagram?

b) How many moles of product can be formed from the reaction of 1.0 mol of $\mathrm{A_2\,(g)}$ and 2.5 mol of $\mathrm{B\,(g)}$?

Answer available at the end of this section.

Exercise $1.E.52$

A student writes the word “chemistry” on paper using a pencil containing graphite, which is pure carbon. The word uses about 0.0045 g of graphite. How many carbon atoms are in the word “chemistry” written in graphite?

Answer available at the end of this section.

Answers

Exercise $1.E.1$

From the label:

2.0 L = 67.6 fl oz

We can write a conversion factor based on this relationship:

$$\left(\frac{67.6\text{ fl oz}}{2.0\text{ L}}\right) = 33.8\text{ fl oz/L}$$

Since 2.0 L has only two significant figures, the conversion factor is limited to two significant figures as well:

$$\left(\frac{34\text{ fl oz}}{1.0\text{ L}}\right)$$

The conversion factor based on the label is: 1.0 L = 34 fl oz (2 sig figs).

Exercise $1.E.2$

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

mass = 132.6 g

volume = 61.2 mL - 48.6 mL = 12.6 mL

$$\frac{132.6\text{ g}}{12.6\text{ mL}} = 10.5\text{ g/mL}$$

Exercise $1.E.3$

$$0.214\ \cancel{\text{mL}}\left(\frac{0.8765\text{ g}}{1\ \cancel{\text{mL}}}\right) = 0.187571\text{ g}$$

Round to three significant figures (based on 0.214 mL): 0.188 g

The chemist should weigh out 0.188 g of benzene.

Exercise $1.E.4$

(a) 2.15×10^5 → 3 significant figures

(b) 4.2×10^6 → 2 significant figures

(c) 2.08 → 3 significant figures

(d) 0.19 → 2 significant figures

(e) 27440 → rounded to the ones place

(f) 43.0 → rounded to tenths place

Exercise $1.E.5$

To convert the beetle's speed from cm/s to km/h:

$$4.20\ \cancel{\text{cm}}/\cancel{\text{s}} \times \left(\frac{1\ \cancel{\text{m}}}{100\ \cancel{\text{cm}}}\right) \times \left(\frac{1\ \text{km}}{1000\ \cancel{\text{m}}}\right) \times \left(\frac{3600\ \cancel{\text{s}}}{1\ \text{h}}\right) = 0.1512\ \text{km/h}$$

Rounded to three significant figures:

$$0.151\ \text{km/h}$$

The beetle moves at a speed of 0.151 km/h.

Exercise $1.E.6$

a)

$$5.2 \times 10^{-4}\ \mu\text{m}^3 \left(\frac{\text{m}^3}{(10^6)^3\ \mu\text{m}^3}\right) \left(\frac{(1000)^3\text{mm}^3}{\text{m}^3}\right) = 5.2 \times 10^{-13}\ \text{mm}^3$$

b)

$$5.2 \times 10^{-13}\ \text{mm}^3(10^{10}) \left(\frac{\text{m}^3}{(1000)^3\ \text{mm}^3}\right) \left(\frac{1000\ \text{L}}{\text{m}^3}\right) = 5.2 \times 10^{-9}\ \text{L}$$

Exercise $1.E.7$

$$1.5\ \text{cups} \left(\frac{1\ \text{serving}}{\frac{1}{3}\ \text{cups}}\right) \left(\frac{20\ \text{mg Ca}}{1\ \text{serving}}\right) = 90\ \text{mg Ca}$$

Exercise $1.E.8$

Similarities:

- Both electrons and protons are subatomic particles that are part of the atom.
- Both carry an electric charge and play a role in the atom's structure and behaviour.

Differences:

- Electrons have a -1 charge, while protons have a +1 charge.
- Protons are much more massive than electrons.
- Protons are located in the nucleus, while electrons are outside the nucleus.

Exercise $1.E.9$

Protons: 53 (from iodine's atomic number on the periodic table)

The mass number (number on top left) gives the number of protons and neutrons together. Neutrons: 131–53=78

Electrons: 53 (same as protons in a neutral atom)

Exercise $1.E.10$

To find the element, look up the atomic number on the periodic table. The mass number goes to the upper left, and the charge goes to the upper right of the element symbol.

a) Atomic number 55 → Cs

Mass number = 133

Charge = +1

$^{133}\text{Cs}^{+}$

b) Number of protons = Atomic number = 53 → I

Mass number = # protons + # neutrons = 53 + 74 = 127

The charge can be determined by comparing the number of protons (53) and electrons (54). Since there is one more electron than proton, the charge is -1:

$^{127}\text{I}^{-}$

c) Atomic number = 15 → P

Mass number = 31

Charge = 3-

$^{31}\text{P}^{3-}$

d) Since the ion has 24 electrons and a 3+ charge, there must be 27 protons (3 more than electrons due to +3 charge).

Atomic number = 27 → Co

Mass number = # protons + # neutrons = 27 + 30 = 57

$^{57}\text{Co}^{3+}$

Exercise $1.E.11$

Molar mass of Mg = 24.31 g/mol

$$0.250\ \text{mol} \left(\frac{24.31\ \text{g}}{\text{mol}}\right) = 6.08\ \text{g Mg}$$

Exercise $1.E.12$

Molar mass of Si = 28.09 g/mol

$$14.0\ \text{g}\left(\frac{\text{mol}}{28.09\ \text{g}}\right) = 0.498\ \text{mol Si}$$

Exercise $1.E.13$

Molar mass of gold (Au) = 197.0 g/mol

First convert from g to mol, using the molar mass, and then from mol to atoms, using Avogadro's number:

$$0.35\ \text{g}\left(\frac{\text{mol}}{197.0\ \text{g}}\right)\left(\frac{6.022 \times 10^{23}\ \text{atoms}}{\text{mol}}\right) = 1.1 \times 10^{21}\ \text{atoms}$$

Exercise $1.E.14$

Molar mass of aluminum (Al) = 26.98 g/mol

First convert from atoms to mol, using Avogadro's number, and then from mol to g, using the molar mass:

$$2.31 \times 10^{21}\ \text{atoms}\left(\frac{\text{mol}}{6.022 \times 10^{23}\ \text{atoms}}\right)\left(\frac{26.98\ \text{g}}{\text{mol}}\right) = 0.103\ \text{g Al}$$

Exercise $1.E.15$

Ionic compounds typically form between metals and nonmetals.

Covalent compounds typically form between two nonmetals.

KCl → Ionic
(Potassium is a metal; chlorine is a nonmetal)

NCl_3 → Covalent
(Nitrogen and chlorine are both nonmetals)

ICl → Covalent
(Iodine and chlorine are both nonmetals)

MgCl_2 → Ionic
(Magnesium is a metal; chlorine is a nonmetal)

PCl_5 → Covalent
(Phosphorus and chlorine are both nonmetals)

CCl_4 → Covalent
(Carbon and chlorine are both nonmetals)

Exercise $1.E.16$

a. Ca^{2+} and S^{2-} have equal and opposite charges, so they combine in a 1:1 ratio:

CaS

b. Al^{3+} needs three Br^{-} to balance the charge:

AlBr_3

c. O^{2-} needs two Na^{+} to balance the charge:

Na_2O

Exercise $1.E.17$

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2–, would give us six negative charges. The formula would be Al_2O_3.

Exercise $1.E.18$

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. However, oxygen gas exists as molecules that contain two oxygen atoms. The formula O_2 shows that each molecule has two oxygen atoms, which is indicated by the subscript 2.

Exercise $1.E.19$

a) They all contain the same number of molecules. One mole of any substance contains the same number of particles, Avogadro's number, 6.022×10^{23} molecules. So, 1 mole of H_2, O_2, and F_2 each contain 6.022×10^{23} molecules.

b)F_2 has the greatest mass. Although all three samples contain 1 mole of molecules, the molar masses of the molecules are different. H_2 has a molar mass of about 2.02 g/mol, O_2 is about 32.00 g/mol, and F_2 is about 38.00 g/mol. Since F_2 has the highest molar mass, 1 mole of F_2 has the greatest mass.

Exercise $1.E.20$

To convert grams to moles, use the molar mass of leucine.

Molar mass of leucine, $\text{C}_6\text{H}_{13}\text{NO}_2$:

- Carbon (C): $6 \times 12.01 = 72.06\ \text{g/mol}$
- Hydrogen (H): $13 \times 1.008 = 13.104\ \text{g/mol}$
- Nitrogen (N): $1 \times 14.01 = 14.01\ \text{g/mol}$
- Oxygen (O): $2 \times 16.00 = 32.00\ \text{g/mol}$

Total molar mass = $72.06 + 13.10 + 14.01 + 32.00 = 131.17\ \text{g/mol}$

Now, convert grams to moles:

$$\text{moles of leucine} = \frac{1.1\ \text{g}}{131.17\ \text{g/mol}} = 0.0084\ \text{mol}$$

Exercise $1.E.21$

a) Use Avogadro's number to convert moles to molecules:

$$7.5 \times 10^{-3}\ \text{mol} \times 6.022 \times 10^{23}\ \frac{\text{molecules}}{\text{mol}} = 4.5 \times 10^{21}\ \text{molecules}$$

b) Use the molar mass to convert moles to grams:

$$7.5 \times 10^{-3}\ \text{mol} \times 64,456\ \frac{\text{g}}{\text{mol}} = 483.42\ \text{g} = 4.8 \times 10^{2}\ \text{g}$$

Exercise $1.E.22$

a. First, calculate the molar mass of glycine, $C_2H_5NO_2$:

- Carbon: $2 \times 12.01 = 24.02$ g/mol
- Hydrogen: $5 \times 1.008 = 5.04$ g/mol
- Nitrogen: $1 \times 14.01 = 14.01$ g/mol
- Oxygen: $2 \times 16.00 = 32.00$ g/mol

Total molar mass = $24.02 + 5.04 + 14.01 + 32.00 = 75.07$ g/mol

Now convert grams to moles:

$$\frac{0.125 \text{ g}}{75.07 \text{ g/mol}} = 0.00166 \text{ mol}$$

b. There are 2 carbon atoms in each molecule of glycine, so for every 1 mole of glycine, there are 2 moles of carbon atoms. We can use this ratio and the molar mass of carbon to calculate the mass of carbon:

$$0.00166 \text{ mol glycine} \left(\frac{2 \text{ mol C}}{1 \text{ mol glycine}}\right) (12.01 \text{ g/mol}) = 0.0399 \text{ g C}$$

Exercise $1.E.23$

A chemical equation is balanced when it shows the same number of atoms of each element on both sides of the reaction. This is important because it ensures the equation follows the law of conservation of matter, which states that matter cannot be created or destroyed in a chemical reaction.

Exercise $1.E.24$

a. $PCl_5(s) + H_2O(l) \rightarrow POCl_3(l) + 2\,HCl(aq)$

b. $H_2(g) + I_2(s) \rightarrow 2\,HI(s)$

c. $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$

d. $2\,Na(s) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + H_2(g)$

e. $P_4(s) + 6\,Cl_2(g) \rightarrow 4\,PCl_3(l)$

f. $PtCl_4(s) \rightarrow Pt(s) + 2\,Cl_2(g)$

Exercise $1.E.25$

We can use the coefficients in the balanced chemical reaction to relate the amounts of $TiCl_4$ and H_2O needed in the reaction:

$$\frac{2 \text{ mol } H_2O}{1 \text{ mol } TiCl_4}$$

$$0.35 \text{ mol } TiCl_4 \left(\frac{2 \text{ mol } H_2O}{1 \text{ mol } TiCl_4}\right) = 0.70 \text{ mol } H_2O$$

Exercise $1.E.26$

Start by converting grams of $Pb(OH)_2$ to moles, then use the mole ratio to find moles of Pb:

$$125.2 \text{ g } Pb(OH)_2 \left(\frac{\text{mol}}{241.21 \text{ g}}\right) \left(\frac{2 \text{ mol Pb}}{2 \text{ mol } Pb(OH)_2}\right) = 0.5190 \text{ mol Pb}$$

Exercise $1.E.27$

Convert grams of aluminum to moles, use the mole ratio to find moles of $Al_2(SO_4)_3$, then convert to grams:

$$13.2 \text{ g Al} \left(\frac{\text{mol}}{26.98 \text{ g}}\right) \left(\frac{1 \text{ mol } Al_2(SO_4)_3}{2 \text{ mol Al}}\right) \left(\frac{342.2 \text{ g}}{\text{mol}}\right) = 83.7 \text{ g } Al_2(SO_4)_3$$

Exercise $1.E.28$

(a) Convert grams of $K[Ag(CN)_2]$ to moles, then use the mole ratio:

$$35.27 \text{ g } K[Ag(CN)_2] \times \frac{1 \text{ mol}}{199.00 \text{ g}} \times \frac{1 \text{ mol } Zn(CN)_2}{2 \text{ mol } K[Ag(CN)_2]} = 0.08862 \text{ mol } Zn(CN)_2$$

(b) Convert moles to molecules:

$$0.08862 \text{ mol } Zn(CN)_2 \times \left(6.022 \times 10^{23} \text{ molecules/mol}\right) = 5.337 \times 10^{22} \text{ molecules}$$

(c) Convert moles to grams using the molar mass of $Zn(CN)_2$ (117.44 g/mol):

$$0.08862 \text{ mol } Zn(CN)_2 \times \frac{117.44 \text{ g}}{1 \text{ mol}} = 10.41 \text{ g}$$

Exercise $1.E.29$

Find the moles of N_2:

$$73.6 \text{ L} \left(\frac{1.25 \text{ g}}{\text{L}}\right) \left(\frac{\text{mol}}{28.01 \text{ g}}\right) = 3.28 \text{ mol } N_2$$

Use the mole ratio and then molar mass to find the mass of sodium azide:

$$3.28 \text{ mol } N_2 \left(\frac{2 \text{ mol } NaN_3}{3 \text{ mol } N_2}\right) (65.01 \text{ g/mol}) = 142 \text{ g}$$

Exercise $1.E.30$

Find how much product can be made if each reactant reacts completely:

$$0.25 \text{ mol } Al(OH)_3 \left(\frac{1 \text{ mol } AlBr_3}{1 \text{ mol } Al(OH)_3}\right) = 0.25 \text{ mol } AlBr_3$$

$$0.80 \text{ mol HBr} \left(\frac{1 \text{ mol } AlBr_3}{3 \text{ mol HBr}}\right) = 0.27 \text{ mol } AlBr_3$$

Since less product can be formed from the $Al(OH)_3$, it runs out first and therefore limits the amount of product that forms. $Al(OH)_3$ is the limiting reactant.

There is more than enough HBr to react with all of the $\mathrm{Al(OH)_3}$, so it is present in excess.

Exercise $1.E.31$

Balance the equation:

$$6\,\mathrm{Li} + \mathrm{N_2} \rightarrow 2\,\mathrm{Li_3N}$$

Find the number of moles of $\mathrm{Li_3N}$ that can be formed from each reactant:

$$1.50\ \mathrm{g\ Li}\left(\frac{1\ \mathrm{mol}}{6.94\ \mathrm{g}}\right)\left(\frac{2\ \mathrm{mol\ Li_3N}}{6\ \mathrm{mol\ Li}}\right) = 0.0720\ \mathrm{mol\ Li_3N}$$

$$1.50\ \mathrm{g\ N_2}\left(\frac{1\ \mathrm{mol}}{28.02\ \mathrm{g}}\right)\left(\frac{2\ \mathrm{mol\ Li_3N}}{1\ \mathrm{mol\ N_2}}\right) = 0.107\ \mathrm{mol\ Li_3N}$$

Li is the limiting reactant, because it runs out first.

Exercise $1.E.32$

Find the number of moles of $\mathrm{CrPO_4}$ that can be formed from each reactant:

$$0.50\ \mathrm{g\ Cr}\left(\frac{1\ \mathrm{mol}}{52.00\ \mathrm{g}}\right)\left(\frac{2\ \mathrm{mol\ CrPO_4}}{2\ \mathrm{mol\ Cr}}\right) = 0.0096\ \mathrm{mol\ CrPO_4}$$

$$0.75\ \mathrm{g\ H_3PO_4}\left(\frac{1\ \mathrm{mol}}{97.99\ \mathrm{g}}\right)\left(\frac{2\ \mathrm{mol\ CrPO_4}}{2\ \mathrm{mol\ H_3PO_4}}\right) = 0.0077\ \mathrm{mol\ CrPO_4}$$

Less $\mathrm{CrPO_4}$ can be produced from $\mathrm{H_3PO_4}$, so $\mathrm{H_3PO_4}$ is the limiting reactant.

To find the mass of $\mathrm{CrPO_4}$, start with the moles of $\mathrm{CrPO_4}$ produced by the limiting reactant and use the molar mass of $\mathrm{CrPO_4}$:

$$0.0077\ \mathrm{mol\ CrPO_4}\left(\frac{146.97\ \mathrm{g}}{\mathrm{mol}}\right) = 1.1\ \mathrm{g}$$

Exercise $1.E.33$

Calculate the theoretical yield:

$$1.31\ \mathrm{g\ CaCO_3}\left(\frac{1\ \mathrm{mol}}{100.09\ \mathrm{g}}\right)\left(\frac{1\ \mathrm{mol\ CO_2}}{1\ \mathrm{mol\ CaCO_3}}\right)\left(\frac{44.01\ \mathrm{g}}{\mathrm{mol}}\right) = 0.576\ \mathrm{g\ CO_2}$$

Then, calculate the percent yield for the reaction:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{0.53\ \mathrm{g}}{0.576\ \mathrm{g}} \times 100\% = 92\%$$

Exercise $1.E.34$

a. Identify the limiting reactant by seeing how much product each reactant can produce:

$$0.200\ \mathrm{mol\ P_4}\left(\frac{1\ \mathrm{mol\ P_4O_{10}}}{1\ \mathrm{mol\ P_4}}\right) = 0.200\ \mathrm{mol\ P_4O_{10}}$$

$$0.200\ \mathrm{mol\ O_2}\left(\frac{1\ \mathrm{mol\ P_4O_{10}}}{5\ \mathrm{mol\ O_2}}\right) = 0.0400\ \mathrm{mol\ P_4O_{10}}$$

$\mathrm{O_2}$ is the limiting reactant.

b. Calculate the theoretical yield of $\mathrm{P_4O_{10}}$:

$$0.0400\ \mathrm{mol\ P_4O_{10}}(283.9\ \mathrm{g/mol}) = 11.4\ \mathrm{g}$$

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{10.0\ \mathrm{g}}{11.4\ \mathrm{g}} \times 100\% = 88.0\%$$

Exercise $1.E.35$

The two samples have the same molarity, the same number of moles of salt per litre of solution.

They are different because the 400 mL sample has a greater total volume and therefore contains more total moles of salt than the 200 mL sample. In other words, the concentration is the same, but the larger sample has more solute and more solution overall.

Exercise $1.E.36$

1. Calculate the molar mass of glycine:

$$\text{molar mass of } {}_2\mathrm{CH_5NO_2} = (2 \times 12.01) + (5 \times 1.008) + (1 \times 14.01) + (2 \times 16.00) = 75.07\ \mathrm{g/mol}$$

2. Convert grams to moles:

$$0.000889\ \mathrm{g}\left(\frac{\mathrm{mol}}{75.07\ \mathrm{g}}\right) = 1.184 \times 10^{-5}\ \mathrm{mol}$$

3. Convert volume to litres:

1.05 mL = 0.00105 L

4. Calculate molarity:

$$\frac{1.184 \times 10^{-5}\ \mathrm{mol}}{0.00105\ \mathrm{L}} = 0.0113\ \mathrm{M}$$

Exercise $1.E.37$

Step 1: Find moles of glucose.

$$\mathrm{mol} = M \times V = 0.30\ \mathrm{mol/L} \times 0.500\ \mathrm{L} = 0.15\ \mathrm{mol}$$

Step 2: Calculate the molar mass of glucose, $\mathrm{C_6H_{12}O_6}$.

- Carbon: $6 \times 12.01 = 72.06\ \mathrm{g/mol}$
- Hydrogen: $12 \times 1.008 = 12.10\ \mathrm{g/mol}$
- Oxygen: $6 \times 16.00 = 96.00\ \mathrm{g/mol}$

Total molar mass = $72.06 + 12.10 + 96.00 = 180.16\ \mathrm{g/mol}$

Step 3: Convert moles to grams:

$$0.15 \text{ mol} \times 180.16 \text{ g/mol} = 27 \text{ g}$$

Exercise $1.E.38$

Find the number of moles in the diluted solution:

$$0.250 \frac{\text{mol}}{\text{L}}(1.00 \text{ L}) = 0.250 \text{ mol}$$

Use the concentration of the original solution to find the required volume:

$$\frac{0.250 \text{ mol}}{1.00 \frac{\text{mol}}{\text{L}}} = 0.250 \text{ L}$$

Exercise $1.E.39$

Find the number of moles in the original solution:

$$0.850 \frac{\text{mol}}{\text{L}}(4.12 \text{ L}) = 3.50 \text{ mol}$$

Find molarity after dilution using the new volume:

$$\frac{3.50 \text{ mol}}{10.00 \text{ L}} = 0.350 \text{ M}$$

Exercise $1.E.40$

Find the number of moles in the original solution:

$$0.09988 \frac{\text{mol}}{\text{L}}(0.2255 \text{ L}) = 0.022523 \text{ mol}$$

Find molarity after evaporation using the new volume:

$$\frac{0.022523 \text{ mol}}{0.04500 \text{ L}} = 0.5005 \text{ M}$$

Exercise $1.E.41$

Find moles of NaOH:

$$0.100 \frac{\text{mol}}{\text{L}}(0.0500 \text{ L}) = 0.00500 \text{ mol NaOH}$$

Use the balanced equation to find moles of H_2SO_4:

$$0.00500 \text{ mol NaOH} \left(\frac{1 \text{ mol } \text{H}_2\text{SO}_4}{2 \text{ mol NaOH}}\right) = 0.00250 \text{ mol } \text{H}_2\text{SO}_4$$

Use molarity to find volume of H_2SO_4:

$$0.00250 \text{ mol} \left(\frac{\text{L}}{0.150 \text{ mol}}\right) = 0.0167 \text{ L}$$

Exercise $1.E.42$

a) To find x using the quadratic formula, rearrange the expression in standard form, $ax^2 + bx + c = 0$:

$$\frac{x^2}{0.75 - x} = 0.60$$

$$\frac{x^2}{0.75 - x}(0.75 - x) = (0.60)(0.75 - x)$$

$$\frac{x^2}{\cancel{0.75 - x}} \cancel{(0.75 - x)} = (0.60)(0.75 - x)$$

$$x^2 = (0.60)(0.75 - x)$$

$$x^2 = 0.45 - 0.60x$$

$$x^2 + 0.60x - 0.45 = 0$$

$a = 1$, $b = 0.60$, and $c = -0.45$. Substitute these values into the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.60 \pm \sqrt{(0.60)^2 - (4)(1)(-0.45)}}{(2)(1)}$$

$$x = \frac{-0.60 \pm \sqrt{2.16}}{2}$$

Solve for the positive and negative solutions:

$$x = \frac{-0.60 + \sqrt{2.16}}{2} \approx 0.4348 \approx 0.43$$

$$x = \frac{-0.60 - \sqrt{2.16}}{2} \approx -1.035 \approx -1.0$$

Thus, $x \approx 0.43$ and $x \approx -1.0$.

b) Using your scientific calculator, substitute each solution for x from Part (a) into the original equation to check that both sides are approximately equal:

$$\frac{x^2}{0.75 - x} = 0.60$$

For $x = 0.43$:

$$\frac{(0.43)^2}{0.75 - 0.43} \approx 0.58$$

For $x = -1.0$:

$$\frac{(-1.0)^2}{0.75 - (-1.0)} \approx 0.57$$

Both values are reasonably close to 0.60, confirming that the rounded solutions from Part (a) are reasonable approximations.

Exercise $1.E.43$

a) $[\mathrm{A}]$ decreases with time. The curve becomes less steep, indicating that the concentration decreases more slowly over time.

Both $[\mathrm{B}]$ and $[\mathrm{C}]$ increase with time. Their curves also become less steep, indicating that the concentrations increase more slowly over time.

b) The relationship between $[\mathrm{A}]$ and time is **not** linear, because the slope of the curve is not constant.

Exercise $1.E.44$

a) No, the particle is **not** travelling at a constant speed between 0 s and 8 s. The slope changes at 6 s, indicating that the speed changes.

b) On a distance-versus-time graph, the slope represents the average speed:

$$m = \frac{\Delta y}{\Delta x} \rightarrow v = \frac{\Delta d}{\Delta t}$$

From the graph, the particle travels 30 m between 0 s and 6 s:

$$v = \frac{d_2 - d_1}{t_2 - t_1}$$

$$v = \frac{30\,\mathrm{m} - 0\,\mathrm{m}}{6\,\mathrm{s} - 0\,\mathrm{s}}$$

$$v = \frac{30\,\mathrm{m}}{6\,\mathrm{s}}$$

$$v = 5\,\mathrm{m/s}$$

Therefore, the average speed of the particle from 0 s to 6 s is 5 m/s. Because the graph is a straight line over this interval, the particle is moving at a constant speed during this time.

c) From 6 s to 8 s, the distance traveled remains constant at 30 m:

$$v = \frac{\Delta d}{\Delta t}$$

$$v = \frac{d_2 - d_1}{t_2 - t_1}$$

$$v = \frac{30\,\mathrm{m} - 30\,\mathrm{m}}{8\,\mathrm{s} - 6\,\mathrm{s}}$$

$$v = \frac{0\,\mathrm{m}}{2\,\mathrm{s}}$$

$$v = 0\,\mathrm{m/s}$$

Therefore, the average speed of the particle from 6 s to 8 s is 0 m/s. A slope of zero means that the distance is not changing with time, so the particle is not moving during this interval.

Exercise $1.E.45$

a) To rearrange for b, start by squaring both sides to remove the square root:

$$(y)^2 = (\sqrt{\frac{3ab}{c}})^2$$

$$y^2 = \frac{3ab}{c}$$

To isolate b, multiply both sides by c and divide both sides by $3a$:

$$\frac{3ab}{c}(\frac{c}{3a}) = y^2(\frac{c}{3a})$$

$$\frac{\cancel{3a}\, b}{\cancel{c}}\left(\frac{\cancel{c}}{\cancel{3a}}\right) = y^2\left(\frac{c}{3a}\right)$$

$$b = \frac{cy^2}{3a}$$

Similarly, to rearrange for c, start by squaring both sides to remove the square root:

$$y = \sqrt{\frac{3ab}{c}} \rightarrow y^2 = \frac{3ab}{c}$$

Multiply both sides by c:

$$(c)y^2 = \frac{3ab}{c}(c)$$

$$cy^2 = \frac{3ab}{\cancel{c}}(\cancel{c})$$

Divide both sides by y^2 to isolate c:

$$cy^2\left(\frac{1}{y^2}\right) = 3ab\left(\frac{1}{y^2}\right)$$

$$c\,\cancel{y^2}\left(\frac{1}{\cancel{y^2}}\right) = 3ab\left(\frac{1}{y^2}\right)$$

$$c = \frac{3ab}{y^2}$$

b) Substitute the given values into the equation. Remember to use the dedicated exponent button on your scientific calculator to enter numbers in scientific notation):

$$y = \sqrt{\frac{3ab}{c}}$$

$$y = \sqrt{\frac{(3)(3.43 \times 10^4)(9.20)}{(6.931 \times 10^{-9})}}$$

$$y = 11687016.35$$

The given values of a and b have 3 significant figures, while c has 4 significant figures. The number 3 in the equation is an exact coefficient, and therefore, it does not limit the final answer to 1 significant figure.

Therefore, the answer should be reported with 3 significant figures:

$$y \approx 1.17 \times 10^7$$

Exercise $1.E.46$

a) Solve for x

$\ln(u) - \ln(v) = wx$

$x = \frac{\ln(u) - \ln(v)}{w}$

This can also be written as:

$x = \frac{\ln(u/v)}{w}$

b) Solve for u

$\ln(u/v) = wx$

$e^{\ln(u/v)} = e^{wx}$

$u = ve^{wx}$

c) Calculate x

$x = \frac{\ln(0.840) - \ln(0.210)}{3.50 \times 10^{-2}}$

$x = 39.608$

$x = 39.6$

Exercise $1.E.47$

a) Solve the second equation for n.

$2m - n = 1$

$-n = 1 - 2m$

$n = 2m - 1$

b) Determine m and n using substitution.

Substitute $n = 2m - 1$ into $4m + 3n = 17$.

$4m + 3(2m - 1) = 17$

$4m + 6m - 3 = 17$

$10m = 20$

$m = 2$

$n = 2(2) - 1 = 3$

$m = 2$ and $n = 3$

c) Verify the solution.

First equation:

$4(2) + 3(3) = 8 + 9 = 17$

Second equation:

$2(2) - 3 = 4 - 3 = 1$

Therefore, the solution is $m = 2$ and $n = 3$.

Exercise $1.E.48$

Find the molar mass of sucrose:

$\text{molar mass of } {}_{12}CH_{22}O_{11} = (12 \times 12.01) + (22 \times 1.008) + (11 \times 16.00) = 342.30 \text{ g/mol}$

Use the molar mass to calculate how many grams of sucrose are in 0.0278 mol and then the number of servings:

$$0.0278 \text{ mol } (342.30 \text{ g/mol}) \left(\frac{1 \text{ serving}}{11.0 \text{ g}}\right) = 0.865 \text{ serving}$$

You would need to eat about 87% of a serving to consume 0.0278 mol of sucrose.

Exercise $1.E.49$

Find the moles of $Ba_3(PO_4)_2$ that can form from each reactant:

$$0.250 \frac{\text{mol } BaCl_2}{\text{L}} (0.0450 \text{ L}) \left(\frac{1 \text{ mol } Ba_3(PO_4)_2}{3 \text{ mol } BaCl_2}\right) = 0.00375 \text{ mol } Ba_3(PO_4)_2$$

$$0.200 \frac{\text{mol } Na_3PO_4}{\text{L}} (0.0400 \text{ L}) \left(\frac{1 \text{ mol } Ba_3(PO_4)_2}{2 \text{ mol } Na_3PO_4}\right) = 0.00400 \text{ mol } Ba_3(PO_4)_2$$

Since less $Ba_3(PO_4)_2$ is produced from $BaCl_2$, it is the limiting reactant.

Find mass of $Ba_3(PO_4)_2$ using molar mass:

$$0.00375 \text{ mol} \times 601.93 \text{ g/mol} = 2.26 \text{ g}$$

Exercise $1.E.50$

Step 1: Find how many moles of Cu can be made from each reactant to identify the limiting reactant:

$$1.20 \text{ g Al} \left(\frac{\text{mol}}{26.98 \text{ g}}\right) \left(\frac{3 \text{ mol Cu}}{2 \text{ mol Al}}\right) = 0.0667 \text{ mol Cu}$$

$$5.00 \text{ g } CuSO_4 \left(\frac{\text{mol}}{159.61 \text{ g}}\right) \left(\frac{3 \text{ mol Cu}}{3 \text{ mol } CuSO_4}\right) = 0.0313 \text{ mol Cu}$$

Since $CuSO_4$ produces fewer moles of Cu, it is the limiting reactant.

Step 2: Calculate the mass of copper produced.

$$0.0313 \text{ mol Cu} \times 63.55 \text{ g/mol} = 1.99 \text{ g Cu}$$

Step 3: Calculate how much aluminum reacts (based on limiting reactant):

$$0.0313 \text{ mol Cu} \left(\frac{2 \text{ mol Al}}{3 \text{ mol Cu}}\right) = 0.0209 \text{ mol Al}$$

$$0.0209 \text{ mol Al} \times 26.98 \text{ g/mol} = 0.563 \text{ g Al reacted}$$

Step 4: Calculate the mass of aluminum remaining (excess):

$$1.20 \text{ g Al} - 0.563 \text{ g Al} = 0.637 \text{ g Al remains}$$

Exercise $1.E.51$

a)

$$3\,A_2\,(g) + 6\,B\,(g) \longrightarrow 6\,AB\,(g)$$

$$A_2\,(g) + 2\,B\,(g) \longrightarrow 2\,AB\,(g)$$

In the diagram, $B\,(g)$ is the limiting reactant because there is leftover $A_2\,(g)$ after the reaction.

b) Find how many moles of product can form from each reactant:

$$1.0 \text{ mol } A_2 \left(\frac{2 \text{ mol AB}}{\text{mol } A_2}\right) = 2.0 \text{ mol AB}$$

$$2.5 \text{ mol B} \left(\frac{2 \text{ mol AB}}{2 \text{ mol B}}\right) = 2.5 \text{ mol AB}$$

Since A_2 produces fewer moles of AB, it is the limiting reactant and the maximum amount of product that can form is 2.0 mol of AB.

Exercise $1.E.52$

Step 1: Calculate moles of carbon.

The molar mass of carbon (C) is 12.01 g/mol.

We use:

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}}$$

Given mass = 0.0045 g:

$$0.0045 \text{ g} \times \frac{1 \text{ mol}}{12.01 \text{ g}} = 0.000375 \text{ mol}$$

Step 2: Calculate the number of carbon atoms.

Using Avogadro's number, 6.022×10^{23} atoms/mol:

$$0.000375 \text{ mol} \times 6.022 \times 10^{23} \frac{\text{atoms}}{\text{mol}} = 2.3 \times 10^{20} \text{ atoms}$$

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2: QUANTUM THEORY AND ELECTRONIC STRUCTURE

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2.4: The Wave-Particle Duality of Matter

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2.E: Quantum Theory and Electronic Structure (Exercises)

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2.1: Introduction

Big Power from Tiny Pulses: Quantum Ideas Behind the World's Strongest Lasers

What do lasers, cancer treatments, and eye surgery have in common? They all rely on the principles of quantum mechanics, our framework for understanding how matter and energy behave on very small scales. In this chapter, we'll explore how light and electrons behave, and how these behaviours shape the structure of atoms and molecules.



Figure 2.1.1**:** A graphic with basic facts about Donna Strickland, co-inventor of Chirped Pulse Amplification (CPA). Strickland was co-awarded the Nobel Prize in Physics for this discovery which has enabled high-powered laser pulses that are now employed in a variety of applications including laser eye surgery. Image from Wikimedia Commons with permission under Creative Commons license CC-BY.

One of the most powerful modern applications of quantum theory is the laser. Invented in 1960, lasers emit highly focused light of a single wavelength. This is very different from flashlights or light bulbs, which emit a range of wavelengths that appear white to our eyes. The ability to control light precisely has enabled technologies from barcode scanners to fiber optics to high-precision cutting.

Lasers became extremely useful shortly after they were invented, but researchers were still looking for ways to make them more powerful. They tried to do this by amplifying very short laser pulses; however, when they tried this, the power was so concentrated that it damaged or destroyed the optical components of the laser equipment. In the 1980s, Canadian physicist Dr. Donna Strickland used her understanding of the nature of light to help solve this major challenge in laser physics.

Strickland's solution was chirped pulse amplification (CPA), a technique that works by temporarily stretching the pulse into multiple lower-energy wavelengths before amplification and then compressing them back together. This clever approach made it possible to produce laser pulses with up to 10^{15} W of power, without damaging the system. That's trillions of watts, compared to just 2–20 W for an LED bulb.

This figure shows the change of a wave, after the application of a Femotosecond oscillator, Pulse stretcher, Laser Amplifier, and Pulse Compressor.

Figure 2.1.1**:** A diagram of the basic principle of CPA. The original laser pulse is first stretched, then amplified before being compressed again, resulting in high energy laser pulses that do not destroy optical components. Image reproduced with permission from Nakajima *et al., Applied Sciences* **2015**, *5*(1) under Creative Commons License CC-BY.

CPA transformed high-intensity laser research and earned Strickland the 2018 Nobel Prize in Physics along with her supervisor, Gérard Mourou. This made her only the 3rd woman in history to have been awarded this honour. Today, in addition to allowing researchers to discover more information about optical phenomena, CPA-based lasers are used in laser eye surgery, cancer treatments, and precision manufacturing.

The same quantum principles that explain how lasers work, like energy levels, quantized transitions, and the wave–particle duality of light, also help us understand how electrons are arranged in atoms. In this chapter, you'll learn how scientists use light to probe atomic structure, and how quantum ideas explain the distribution of electrons in atoms and periodic trends in the elements.

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2.2: The Nature of Light

Learning Objectives

- Identify the frequency, amplitude, and wavelength of an electromagnetic wave
- Calculate related properties of light such as frequency, wavelength, and energy
- Explain the wave-particle duality of light

Scientists have learned much about atomic structure by studying how atoms interact with different forms of radiant energy. This includes visible light, which we see with our eyes, infrared radiation, which we feel as heat, ultraviolet light, which causes sunburn, and X-rays, which are used to image bones and teeth. To understand how these interactions help explain atomic structure, we first need to explore the properties of waves and electromagnetic radiation.



Figure 2.2.1: A wave in water. When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a repeating oscillation that carries energy through space. You can see waves when you drop a stone into a pond or when ocean waves move toward a shore (Figure 2.2.1). These waves form when energy is transferred to water, causing its surface to rise and fall as the wave moves outward. A floating object in the water moves up and down as a wave passes but does not travel with the wave itself.

All waves are described by three main properties: wavelength, frequency, and amplitude.

- Wavelength (λ, the lowercase Greek letter lambda) is the distance between two consecutive peaks or troughs in a wave. It is measured in meters (m) in the SI system.
- Frequency (ν, the lowercase Greek letter nu) is the number of wave cycles that pass a specified point in space in a specified amount of time (measured in seconds in the SI system). A cycle corresponds to one complete wavelength. The unit for frequency is expressed as cycles per second (s^{-1}) or hertz (Hz). Common multiples of this unit are megahertz, (1 MHz = 1 × 10^6 Hz) and gigahertz (1 GHz = 1 × 10^9 Hz).
- Amplitude is the height of a wave from its midpoint to a peak or trough (Figure 2.2.2). It is related to a wave's intensity: for light, this determines brightness; for sound, it determines loudness.

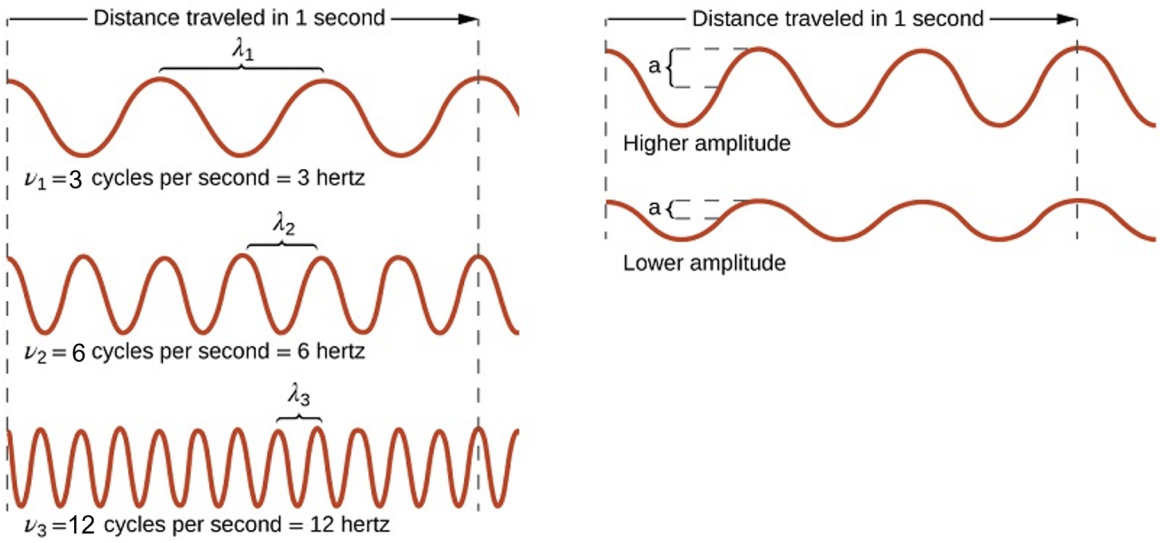


Figure 2.2.2: One-dimensional waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough. (CC BY 4.0; OpenStax)

The distance a wave travels per unit time is its speed, typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = \text{speed} \tag{2.2.1}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{\text{wave}}}{\text{second}}\right) = \frac{\text{meters}}{\text{second}} \tag{2.2.2}$$

Different types of waves may have vastly different speeds and frequencies. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20 °C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by causing matter (water) to oscillate. In contrast, electromagnetic radiation transmits energy through space as oscillating electric and magnetic fields (Figure 2.2.3). These fields move perpendicular to each other and to the direction of wave travel. All forms of electromagnetic radiation—including microwaves, visible light, and gamma rays—travel at the speed of light (c) in a vacuum. This speed is a fundamental constant:

c = 2.99792458 × 10^8 m/s ≈ 3.00×10^8 m/s

This is about a million times faster than the speed of sound.

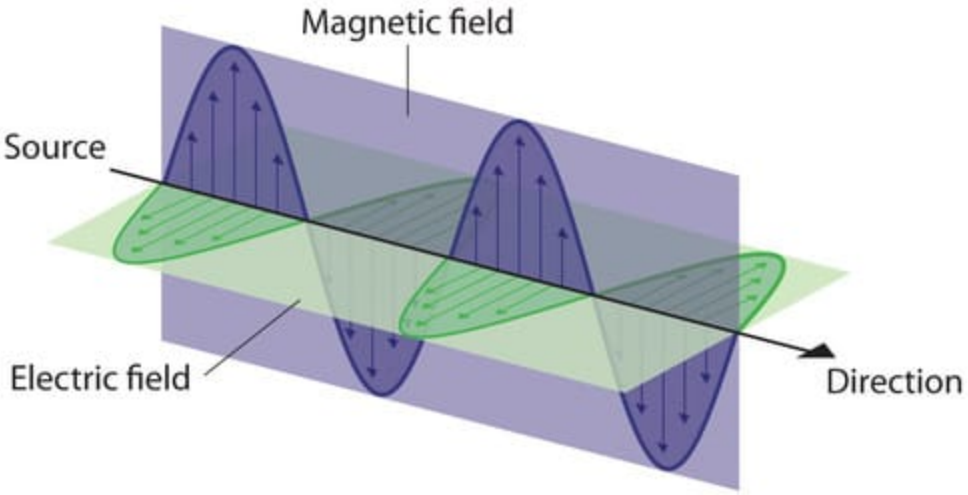


Figure 2.2.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Since all electromagnetic waves travel at the same speed (c), they differ only in wavelength and frequency. As shown in Figure 2.2.4 and Table 2.2.1, the wavelengths of familiar electromagnetic radiation range from 10^{1} m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing the speed (ν) in Equation 2.2.2 with the speed of light (c) gives:

$$c = \lambda\nu \tag{2.2.3}$$

$$\nu = \frac{c}{\lambda} \tag{2.2.4}$$

This equation shows that, since the speed of light is constant, wavelength and frequency are inversely related: when one increases, the other decreases.

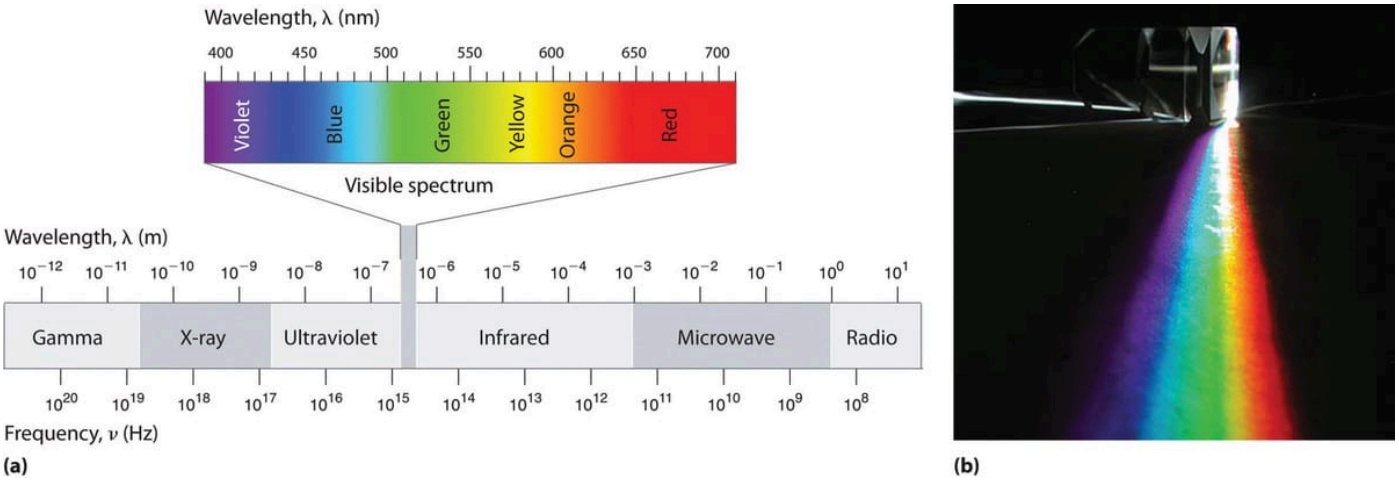


Figure 2.2.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. Notice that the wavelength increases from left to right and the frequency increases from right to left across the spectrum. The visible portion of the electromagnetic spectrum is a narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

The human eye detects only a small part of the electromagnetic spectrum—visible light—with wavelengths between 400 nm (violet) and 700 nm (red). The order of colors follows decreasing wavelength: red, orange, yellow, green, blue, indigo, and violet (ROYGBIV).

White light is a mixture of all visible wavelengths. When passed through a prism, it splits into different colors, as shown in Figure 2.2.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 2.2.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	UV, visible
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

Example 2.2.1: Wavelength of Radiowaves

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101 MHz. What is the wavelength of this radiation? 1 MHz is 10^6 Hz.

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 2.2.4 to calculate the wavelength in meters.

Pay attention to units and make sure they cancel!

Solution:

From Equation 2.2.4, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 3.00×10^8 m/s:

$$\begin{aligned} \lambda\nu &= c \\ &= 3.00 \times 10^8 m/s \end{aligned}$$

Thus the wavelength λ is given by

$$\begin{aligned} \lambda &= \frac{c}{\nu} \\ &= \left(\frac{3.00 \times 10^8 \ m/\cancel{s}}{101 \ \cancel{MHz}}\right)\left(\frac{1 \ \cancel{MHz}}{10^6 \ \cancel{s^{-1}}}\right) \\ &= 2.97 \ m \end{aligned}$$

Example 2.2.2: Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

Given: wavelength

Asked for: frequency

Strategy:

Rearrange the Equation 2.2.4 to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Pay attention to units and make sure they cancel!

Solution Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{3.00 \times 10^{8} \cancel{\text{m}}\,\text{s}^{-1}}{589\,\cancel{\text{nm}}}\right)\left(\frac{1 \times 10^{9}\,\cancel{\text{nm}}}{1\,\cancel{\text{m}}}\right) = 5.09 \times 10^{14}\,\text{s}^{-1}$$

Exercise 2.2.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength in mm of the radiation emitted by the radar gun? (Note: 1 GHz = 10^9 Hz.)

Answer available at the end of this section.

Chemistry in Everyday Life: Wireless Communication







Figure 2.2.5: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the cell tower disguised as a tree on Lake Rousseau in the Muskokas, about 200 km from Toronto, ON. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens; credit right work by E. Boutilier, @edboutilier)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 2.2.6). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

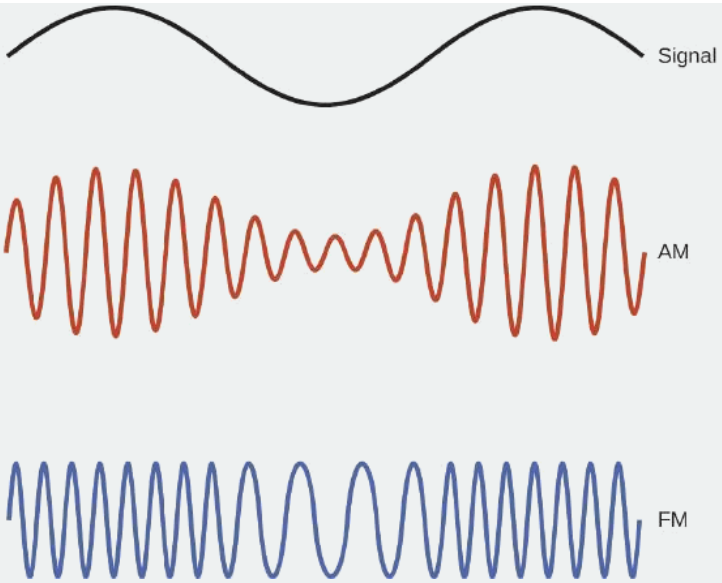


Figure 2.2.6: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

Wave Interference and Diffraction

Like other types of waves, electromagnetic waves can interact when they are near each other. This interaction, called interference, can be either constructive or destructive as shown in Figure 2.2.7. Constructive interference occurs when the peaks of two waves align (in phase). Their amplitudes add together, resulting in brighter light. Destructive interference occurs when the peak of one wave aligns with the trough of another (out of phase). Their amplitudes cancel out partially or completely, leading to a smaller wave or no wave at all.

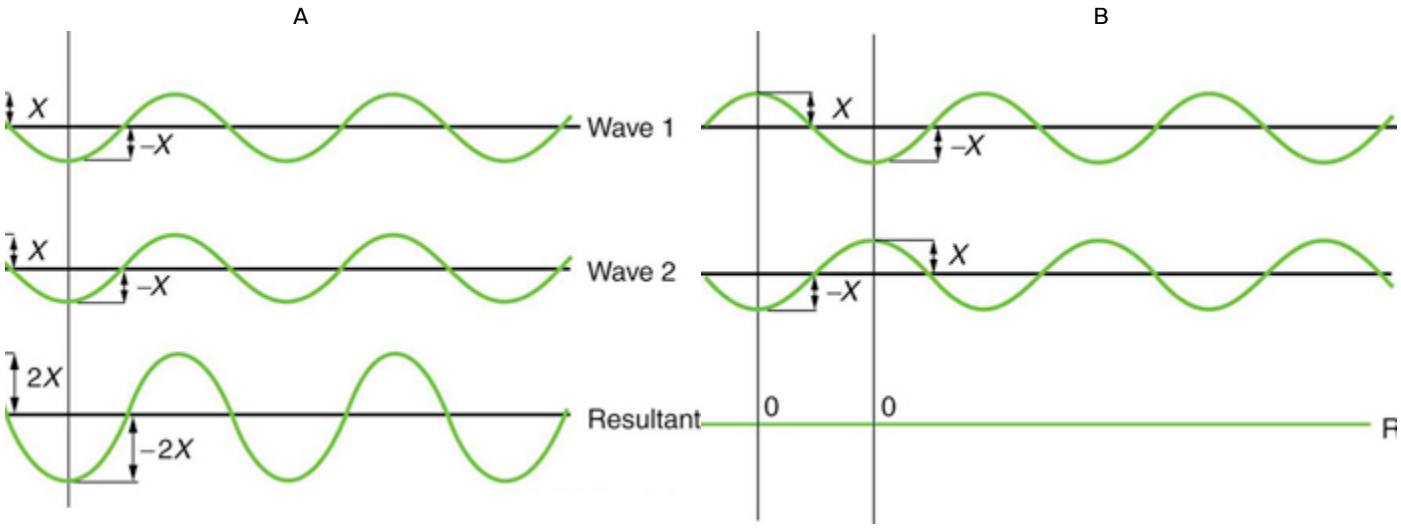


Figure 2.2.7: Constructive interference of two identical waves in phase (A) produces one with twice the amplitude, but the same wavelength. Destructive interference of two identical waves out of phase produces zero amplitude, or complete cancellation (B).

Waves also diffract, meaning they bend when passing through an opening or around an object. In the double slit experiment (Figure 2.2.8), waves pass through two narrow slits in a wall. At each slit, the waves spread out and the resulting semi-circular waves interfere with each other, creating an interference pattern. Brighter regions and darker regions are observed because of constructive and destructive interference respectively. This experiment produces the same interference pattern for water waves and light, suggesting that light behaves as a wave.

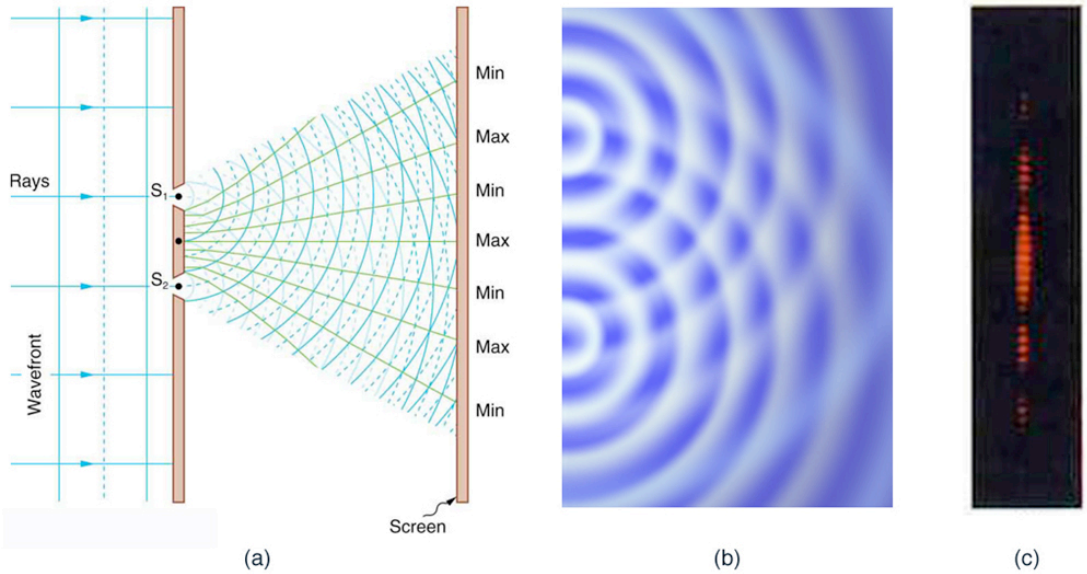


Figure 2.2.8: Double slits produce two sources of waves that interfere. (a) Light spreads out (diffracts) from each slit, because the slits are narrow. These waves overlap and interfere constructively (bright lines) and destructively (dark regions). (b) Double slit interference pattern for water waves are nearly identical to that for light. Wave action is greatest in regions of constructive interference and least in regions of destructive interference. (c) When light that has passed through double slits falls on a detector screen, we see an interference pattern with brighter and darker spots due to interference. (credit: PASCO)

Portrait of a Chemist: Dorothy Crowfoot Hodgkin

X-rays have wavelengths of approximately 0.01–10 nm, which are similar in size to the spaces between atoms in a crystal. When X-rays pass through a crystal, they are scattered by the atoms. The scattered rays interfere, creating a distinct diffraction pattern. By analyzing this pattern, scientists can determine the exact positions of atoms in a crystal. This technique, known as X-ray crystallography, has been essential in determining molecular structures. One of its pioneers was Dorothy Crowfoot Hodgkin.

Born in Cairo, Egypt, in 1910 to British parents, Hodgkin developed a passion for chemistry early in life. At age 11, she was one of only two girls permitted to study chemistry at her prestigious grammar school. On her 16th birthday, her mother gave her a book on X-ray crystallography, sparking her lifelong interest in the field.

Hodgkin earned a first-class honors degree in chemistry from Oxford University (1932) and then pursued a PhD at Cambridge University, where she recognized the potential of X-ray crystallography for studying protein structures. After earning her PhD in 1937, she made groundbreaking contributions to structural chemistry.

Throughout her career, Dr. Hodgkin determined the structures of several essential biomolecules, including cholesterol iodide, penicillin, and vitamin B12. Her achievements in using X-ray techniques to study biochemical substances earned her the 1964 Nobel Prize in Chemistry.

In 1969, she led a team that determined the structure of insulin, paving the way for its mass production and greatly improving the treatment of diabetes. She remained an active member of the international scientific community, receiving numerous honors before her passing in 1993.

The double-slit experiment highlights a key difference between waves and particles. If light were made of particles, we would expect it to behave like tennis balls thrown at a wall with holes—each particle would either pass through a slit or hit the wall. No interference pattern would form. However, the observed diffraction and interference patterns suggest that light has wave-like

properties. While the details of diffraction and interference are beyond the scope of this course, we use these concepts as a way to contrast wave-like and particle-like behavior.

Particle Nature of Light

Until the late 19th century, scientists viewed matter and energy as distinct. However, several puzzling observations challenged this idea. One key discovery was the photoelectric effect, where light shining on a metal surface causes electrons to be ejected (Figure 2.2.9). Classical physics predicted that the number of electrons ejected and their kinetic energy should depend on only the intensity of the light, not its frequency.

However, experiments showed a different result:

- Each metal has a threshold frequency—below this frequency, no electrons are ejected, regardless of intensity.
- Above the threshold frequency, the number of ejected electrons is proportional to light intensity, but their kinetic energy depends on frequency, not amplitude.

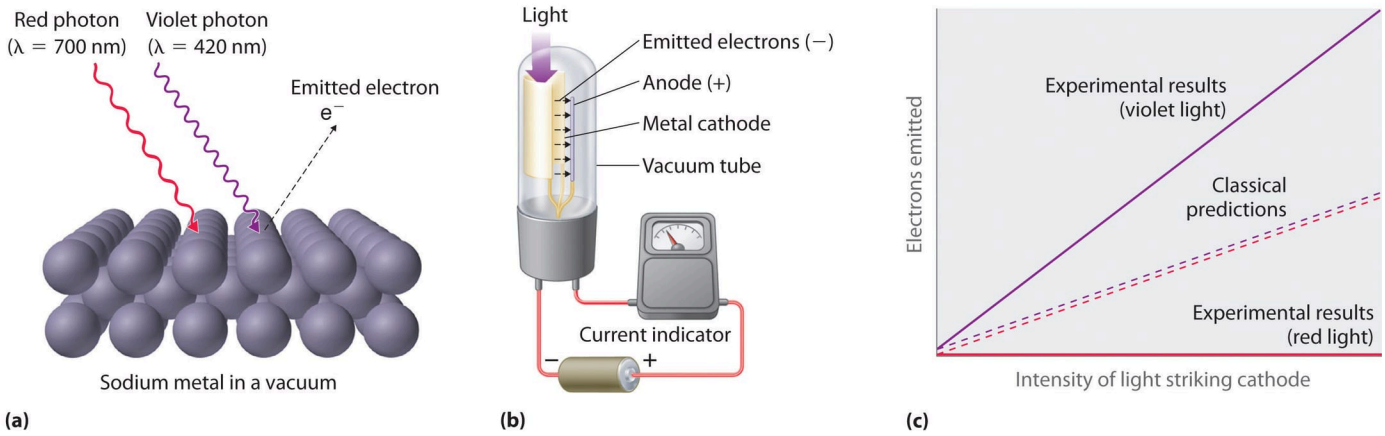


Figure 2.2.9: The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are ejected and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to classical physics predictions, no electrons are ejected when photons of light with energy less than the threshold frequency, such as red light, strike the cathode. The frequency of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.*

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) explained the photoelectric effect using quantization of light. He proposed that radiant energy is not continuous but comes in discrete packets called photons. The energy of a photon is directly proportional to the frequency of light:

$$E_{photon} = h\nu \tag{2.2.5}$$

where h is Planck's constant, 6.626 × 10^{-34} joule seconds (J s). Since frequency and wavelength are inversely related, photon energy can also be expressed as:

$$E = \frac{hc}{\lambda} \tag{2.2.6}$$

These equations describe the energy of a single photon using either its frequency (Equation 2.2.5) or its wavelength (Equation 2.2.7), which are essentially interchangeable since the speed of light is constant. When we experience visible electromagnetic radiation, the energy of each photon (which can be described using wavelength or frequency) determines the colour that we see. The brightness of the light is determined by how many photons are present, something that is characterized by the amplitude of the wave or often referred to as the intensity of the radiation.

In the photoelectric effect, each metal has a binding energy that must be overcome for an electron to be ejected (binding energy is also called threshold energy or ionization energy as it's the energy required to remove an electron and turn the atom into an ion). If photons of light with energy less than the binding energy strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are ejected regardless of the intensity of the light. If a photon with energy greater than the

binding energy strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron. Calculations involving the photoelectric effect are beyond the scope of CHM 135H, but Equation 2.2.7, based on the conservation of energy, is useful to develop your conceptual understanding.

$$kinetic\ energy\ of\ ejected\ electron = E_{photon} - binding\ energy \tag{2.2.7}$$

When a metal is struck by light with energy above the threshold energy or binding energy, the *number* of ejected electrons is proportional to the *intensity* of the light beam, which is related to the number of photons. The *kinetic energy* of the ejected electrons is proportional to the *frequency* of the light because one electron absorbs the energy of one photon and so if the energy of the photon is greater than the binding energy this excess energy is transformed into increased kinetic energy of that electron.

Einstein's discovery deepened the mystery of light's nature. Wave behavior explains phenomena like interference and diffraction (e.g., the double-slit experiment), while particle behavior explains phenomena like the photoelectric effect. Since light exhibits both wave-like and particle-like properties, it cannot be fully described as just a wave or just a particle. This concept, known as wave-particle duality, remains a fundamental idea in modern physics.

Example 2.2.3: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photons being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34}\ \text{J}\cancel{\text{s}})(3.00 \times 10^{8}\ \text{m}\cancel{\text{s}^{-1}})}{(640\ \cancel{\text{nm}}) \left(\dfrac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}} \right)} \\ &= 3.11 \times 10^{-19}\ \text{J} \end{aligned}$$

Exercise 2.2.2

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven - they do not contain water molecules.) This frequency is about 3 × 10^9 Hz. What is the energy of one photon in these microwaves?

Answer available at the end of this section.

Example 2.2.4: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
c. True if the energy of the light is greater than the binding energy. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases. (If the energy of the light is less than the binding energy, no electrons would be ejected regardless of the brightness.)
d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Summary

Understanding the electronic structure of atoms requires knowledge of waves and electromagnetic radiation:

Waves are periodic oscillations that transmit energy. Waves are characterized by several interrelated properties:

- Wavelength (λ): Distance between successive waves.
- Frequency (ν): Number of waves passing a point per second.
- Speed: Rate at which waves propagate.
- Amplitude: Height of the wave

The speed of a wave is equal to the product of its wavelength and frequency.

Electromagnetic radiation consists of perpendicular electric and magnetic fields moving at the speed of light. It includes radio waves, microwaves, visible light, X-rays, and gamma rays, which differ in wavelength and frequency. The energy of a photon, a particle of light, is proportional to the frequency of light and inversely proportional to the wavelength of light. Electromagnetic waves show wave-particle duality exhibiting wave properties such as interference and diffraction and also particle properties. This dual nature of light is essential to understanding atomic structure and modern quantum theory.

Glossary

amplitude
: The extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude).

binding energy
: The minimum energy required to remove an electron from an atom, result in an ion; also called ionization energy or threshold energy.

constructive interference
: Occurs when the peaks of two electromagnetic waves align ("in phase") and their amplitudes add together, resulting in brighter light.

destructive interference
: Occurs when the peak of one electromagnetic wave aligns with the trough of another ("out of phase") and their amplitudes cancel out, resulting in a smaller wave or no wave.

diffraction
: Redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions.

double slit experiment
: An investigation into the diffraction of light when waves pass through narrow slits, resulting in an interference pattern showing that light behaves as a wave.

electromagnetic radiation
Energy transmitted by waves that have an electric-field component and a magnetic-field component.

electromagnetic spectrum
The range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths.

frequency (ν)
The number of wave cycles that pass a specified point in space in a specified amount of time; unit expressed as cycles per second (s^{-1}) or hertz (Hz).

hertz (Hz)
The SI unit of frequency, which is the number of cycles per second, s^{-1}.

interference pattern
A pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves.

kinetic energy
The energy of motion.

photoelectric effect
The ejection of electrons from a metal's surface when irradiated by light above its threshold frequency.

quantization
Occurring only in specific discrete values, not continuous.

speed
The distance a wave travels per unit time, measured in meters per second (m/s); the speed of a wave is equal to the product of its wavelength and frequency.

threshold frequency
The frequency of light shone at a metal below which no electrons are ejected and above which the number of ejected electrons is proportional to light intensity.

wave
An oscillation that can transport energy from one point to another in space.

wavelength (λ)
The distance between two consecutive peaks or troughs in a wave.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 2.2.1

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \left(\frac{3.00 \times 10^8\ m/\cancel{s}}{35.5\ \cancel{GHz}}\right)\left(\frac{1\ \cancel{GHz}}{10^9\ \cancel{s^{-1}}}\right) \\ &= 0.00845\ m\end{aligned}$$

8.45 mm

Exercise 2.2.2

2×10^{-24} J

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2.3: Atomic Spectra

Learning Objectives

- Relate atomic spectra to the electronic structure of the hydrogen atom
- Calculate the energies, frequencies, and wavelengths of photons absorbed and emitted by electronic transitions in the hydrogen atom

Another experiment that challenged existing scientific models was atomic spectra, the light emitted when an element is vaporized and excited electrically. Atomic spectra provided direct evidence that energy in matter is quantized. This section explores how observations of atoms interacting with visible light supported this idea.

Line Spectra

Objects at high temperatures emit a continuous spectrum of electromagnetic radiation. However, when pure elements are heated, they produce a different type of spectrum. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the H_2 molecules dissociate into hydrogen atoms which emit a red light. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a line spectrum, are observed rather than a continuous range of wavelengths (Figure 2.3.1). The light emitted by hydrogen atoms is red because, of its four characteristic lines in the visible region, the most intense line is in the red portion of the visible spectrum, at 656 nm.

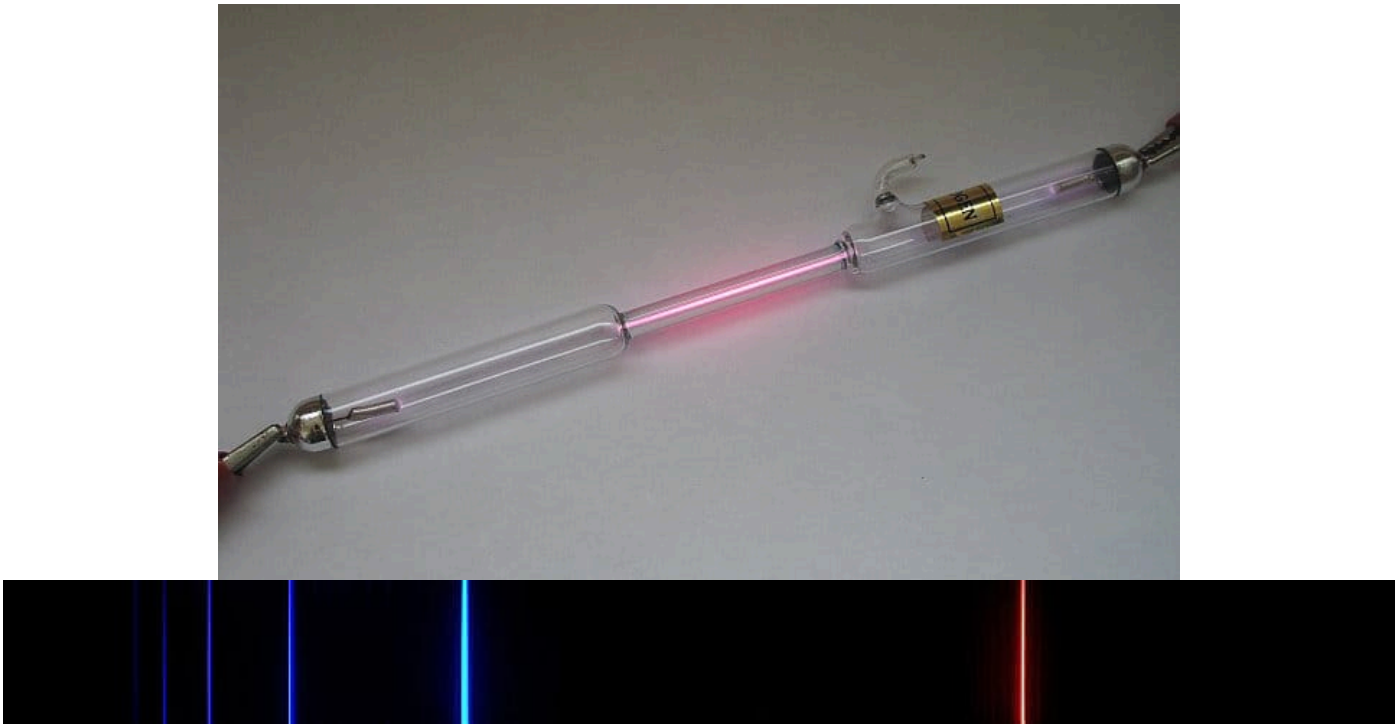


Figure 2.3.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; Science Made Alive via Wikipedia) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed in the visible region, the most intense of which is at 656 nm. (CC BY-SA 3.0; Jan Homann via Wikipedia)

Each element produces a unique set of spectral lines (Figure 2.3.2), as do molecules, although their spectra are generally much more complicated. For example, the red glow of neon signs used in advertising comes from the emission spectrum of neon. By the late 19th century, scientists had observed emission spectra for many elements, but classical physics could not explain these patterns.

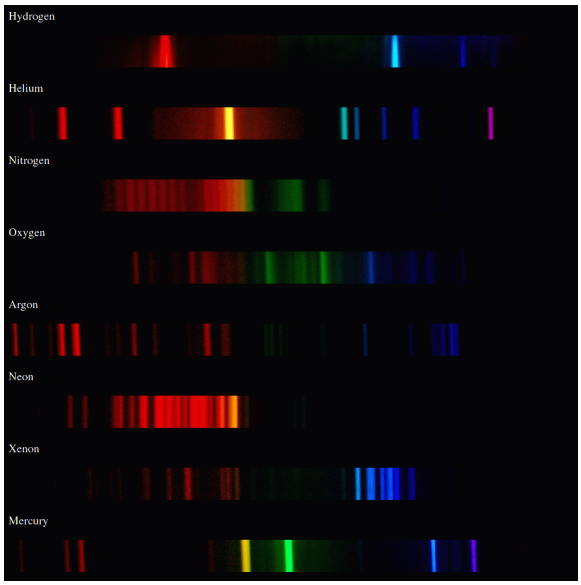


Figure 2.3.2: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. Astronomical spectra image(opens in new window) from the Rochester Institute of Technology, CC BY-NC-SA 2.0(opens in new window).

In the case of hydrogen, the fact that only specific wavelengths (or frequencies) appear in its spectrum means that only certain energies of light are emitted. This led to a key conclusion:

- The energy levels of a hydrogen atom must be quantized—only certain energy values are possible.

If the energy levels in a hydrogen atom were not quantized, its spectrum would be continuous rather than consisting of distinct lines. While scientist recognized this must be true, classical physics could not explain why this was the case. During the late 1800s, scientists developed mathematical equations to describe the hydrogen spectrum, but they did not understand why these equations worked.

Bohr's Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model to explain the hydrogen emission spectrum. Bohr's model introduced the idea that electrons orbit the nucleus in circular paths with specific, allowed radii. Bohr assumed that an electron does not emit energy while in a stable orbit. However, an electron would emit or absorb energy when moving between orbits. The energy of the absorbed or emitted light must equal the difference between the two energy levels, according to the law of conservation of energy:

$$|\Delta E| = |E_f - E_i| = E_{photon} = h\nu = \frac{hc}{\lambda} \tag{2.3.1}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbit energies, respectively. The absolute value of the energy difference is used because ΔE can be positive or negative depending on whether the atom absorbed or released the photon, however the frequencies and wavelengths of the photon that caused the change is always positive. Instead of allowing continuous energy values, Bohr proposed that electron energies are quantized, meaning they can only exist in specific levels (n = 1, 2, 3,...).

Bohr derived an equation to calculate the energy of each orbit in a hydrogen atom:

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{n^2}\right) \tag{2.3.2}$$

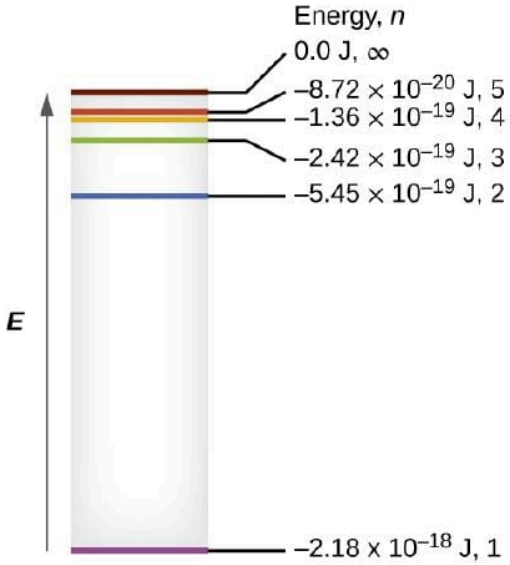


Figure 2.3.3: Energy levels in a hydrogen atom. The more negative the energy value, the lower the energy.

The energy levels for a hydrogen atom are shown in Figure 2.3.3. The $n = 1$ level corresponds to the lowest energy orbit which is closest to the nucleus. A hydrogen atom with its one electron in the $n = 1$ level has the lowest possible energy, which is called the ground state (the most stable arrangement of electrons for an element or a compound).

As n increases, the electron moves further from the nucleus, making the atom less stable. A hydrogen atom with an electron in an orbit with $n > 1$ is in an excited state, defined as any arrangement of electrons higher in energy than the ground state.

In the $n = \infty$ level, the energy holding the electron and the nucleus together is zero. The electron is completely removed from the atom, meaning the atom has ionized.

If an atom absorbs energy, the electron moves to a higher orbit (excited state). When the electron falls back to a lower level, it emits a photon with an energy exactly equal to the difference between the two energy levels. This follows the law of conservation of energy - no energy is lost or gained in the process.

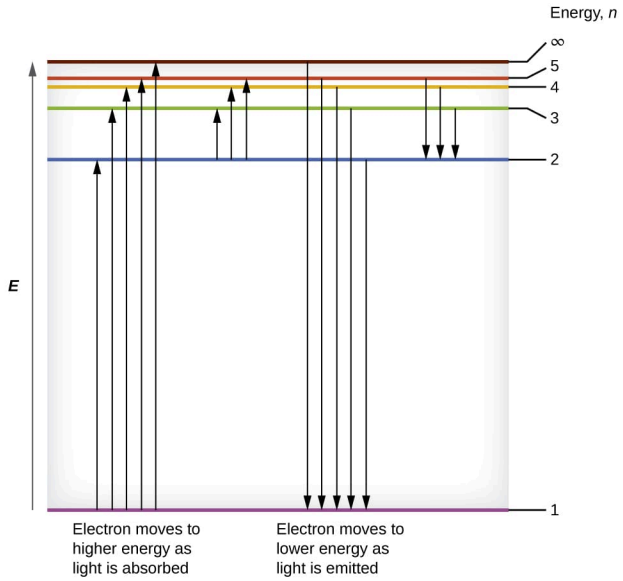


Figure 2.3.4: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

From equation 2.3.2, we can calculate the difference in energy (ΔE) between any two energy levels in the hydrogen atom, $\Delta E = E_{n_f} - E_{n_i}$ where n_f is the final orbit and n_i the initial orbit:

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18} J \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \tag{2.3.3}$$

We can now understand the physical basis for the lines in the emission spectrum of hydrogen (2.3.1*b*); the lines in this series correspond to transitions from higher-energy orbits ($n > 2$) to the second orbit ($n = 2$):

$n = 3 \rightarrow n = 2 \rightarrow 656\text{nm}\,(\text{red})$
$n = 4 \rightarrow n = 2 \rightarrow 486\text{nm}\ (\text{green})$
$n = 5 \rightarrow n = 2 \rightarrow 434\text{nm}\ (\text{blue})$
$n = 6 \rightarrow n = 2 \rightarrow 410\text{nm}\ (\text{violet})$

Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the $n = 3$ than the $n \geq 4$ levels. Consequently, the $n = 3$ to $n = 2$ transition is the most intense line, producing the characteristic red color of a hydrogen discharge (Figure 2.3.1).

These four lines appear in the visible spectrum and are known as the Balmer series. Other series exist for transitions to different levels (Figure 2.3.5): the Lyman series ($n > 1$ to $n = 1$) in the ultraviolet region and the Paschen ($n > 3$ to $n = 3$), Brackett ($n > 4$ to $n = 4$), and Pfund series ($n > 5$ to $n = 5$) in the infrared region.

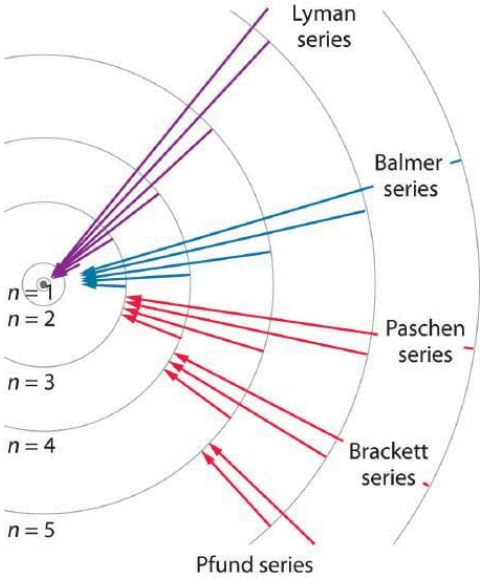


Figure 2.3.5: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit ($n = 1$); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Balmer series of lines are due to transition to $n = 2$ and correspond to light in the visible region. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

Chemistry in Everyday Life: Fireworks

The vibrant colors of fireworks are a direct result of atomic emission spectra. When a firework explodes, the heat from the reaction excites atoms to higher energy levels. As these atoms return to lower energy states, they emit light of specific wavelengths, producing the bright colors we see (Figure 2.3.6).



Figure 2.3.6 :The Chemistry of Fireworks *(a) In the shell used for fireworks, the chambers contain mixtures of fuels and oxidizers plus compounds for special effects ("stars") connected by time-delay fuses so that the chambers explode in stages. (b) The finale of a fireworks display usually consists of many shells fired simultaneously to give a dazzling multicolor display. The labels indicate the substances that are responsible for the colors of some of the fireworks shown.*

A typical firework shell contains gunpowder, which serves two functions: it propels the firework into the air and produces the high temperatures needed to excite metal atoms. These excited atoms then emit light as they return to lower energy levels.

Different metals produce different colors based on their characteristic emission spectra. Sodium gives a bright yellow color due to its 589 nm emission line, but because sodium's yellow light is so intense, potassium and ammonium salts are often used instead when other colors are needed. Strontium compounds emit red, barium salts produce green, and copper compounds give blue light, though achieving a deep, bright blue is particularly challenging. Copper salts can also be hazardous, as they may react with oxidizers to form unstable and explosive compounds.

Because firework colors depend on precise chemical formulations, designing fireworks is both a scientific and artistic challenge. Understanding atomic emission spectra allows chemists to create fireworks that are not only beautiful but also safe and stable.

Absorption Spectra

So far, we have discussed how atoms in excited states emit light, producing an emission spectrum. However, atoms can also absorb light, becoming excited to higher energy levels. This process creates an absorption spectrum, which is essentially the inverse of an emission spectrum.

- Emission spectrum: Light is emitted as an electron moves to a lower energy level.
- Absorption spectrum: Light is absorbed as an electron moves to a higher energy level.

If white light is passed through a sample of hydrogen gas, some wavelengths are absorbed as electrons move to higher energy levels ($n \geq 2$). When this visible light is passed through a prism, a continuous spectrum appears, but with dark lines at specific wavelengths—656, 486, 434, and 410 nm Figure 2.3.7. These correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. These absorption bands are identical to the emission lines (Figure 2.3.7b) as the difference between energy levels is the same whether the electron is moving from lower to higher energy level (absorption) or a higher to lower energy level (emission). If a wider range of wavelengths of light were included in the experiment described, we would see absorption bands at all the energies described by equation 2.3.3, and shown the Figure 2.3.6.

Because each element absorbs and emits light at specific wavelengths, it has a unique emission and absorption spectrum. These spectra are complementary: the dark lines in an absorption spectrum match the bright lines in the emission spectrum.

Emission and absorption spectra form the basis of spectroscopy, a powerful tool for studying the structure and composition of matter.

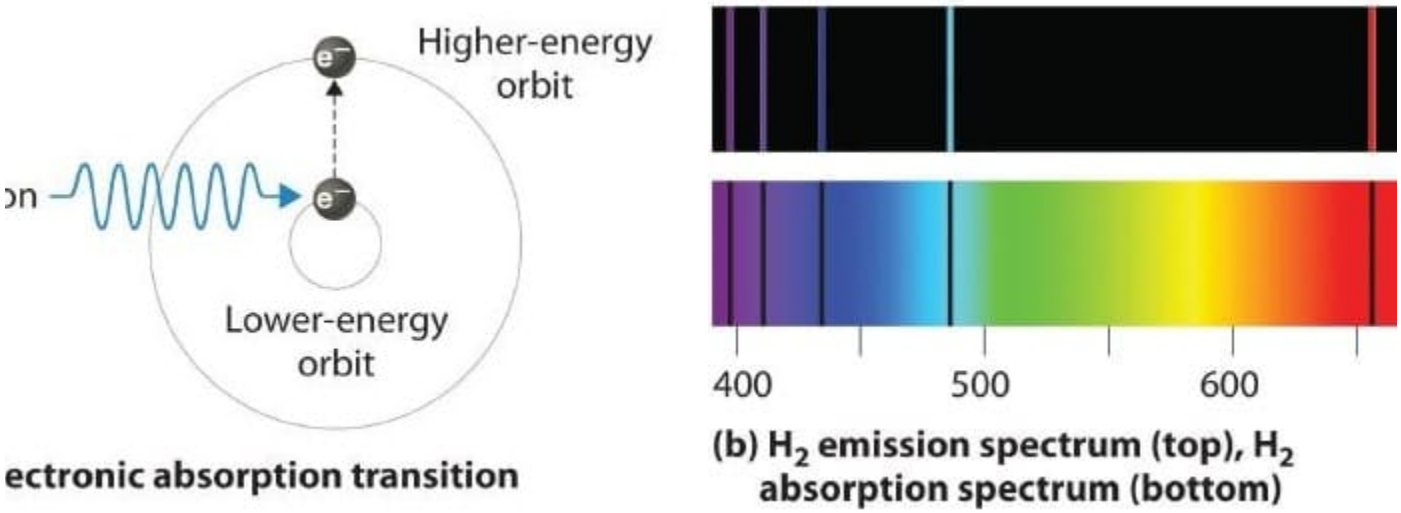


Figure 2.3.7: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC BY-NC-SA 3.0; anonymous)

Chemistry in Everyday Life: Composition of Stars

Astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 2.3.8 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements.

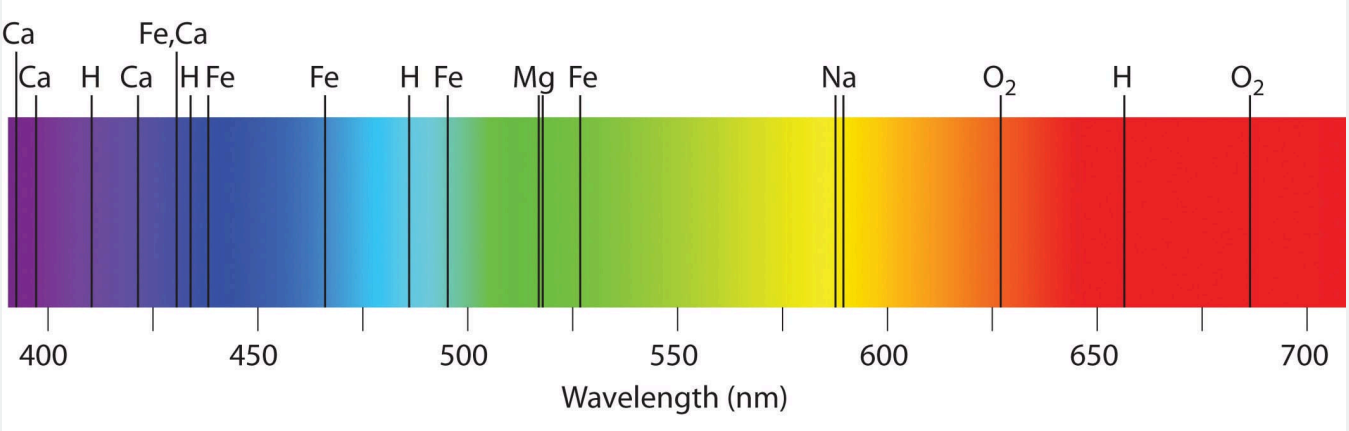


Figure 2.3.8: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere. (CC BY-NC-SA 3.0; anonymous)

Calculations Involving Emission and Absorption Spectra

In this chapter so far we have defined the particle-wave duality of electromagnetic radiation, which allows us to relate the energy of a photon with its wavelength or frequency:

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

We also described the quantization of energy levels in the atom, with particular emphasis on the hydrogen atom where each energy level is described by equation 2.3.2,

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{n^2}\right)$$

and a change in energy levels by equation 2.3.3:

$$\Delta E = -2.18 \times 10^{-18} J \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

These topics come together when calculating aspects of the emission or absorption spectra of the hydrogen atom as the change in energy within the atom is related to the absolute value of the energy of the photon released or absorbed (equation 2.3.1):

$$|\Delta E| = E_{photon}$$

In atomic absorption, a photon is absorbed by an electron in the atom and promoted it to a higher energy level. The atom is now in a higher energy state and so ΔE will be positive. In atomic emission an electron moves from a higher energy level to a lower energy level, the atom is now in a lower energy state and so ΔE is negative, with the energy that was lost released as a photon. In both cases the energy of the photon, whether absorbed or released, is always positive. The two examples below go through these types of calculations and the accompanying thought process in detail.

It is important to note that all atoms can undergo atomic absorption and emission, but the calculations using equations 2.3.2 and 2.3.3 only apply to the hydrogen atom. Subsequent sections of this chapter will discuss the reasons for this in more detail.

Example 2.3.1: Emission spectrum

The Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the $n = 1$ level. What is the wavelength of the lowest-energy line in this series?

Given: lowest-energy transition to $n = 1$

Asked for: wavelength of the photon releases in lowest-energy transition to $n = 1$

Strategy:

A. Consider which transition would release the lowest energy photon.
B. Calculate the energy of the electronic transition which gives the energy of the photon.
C. From the energy of the photon, find the wavelength of the light.

Solution:

A. We are told in the question that all of the transitions in the Lyman series are to the $n = 1$ level, so we know the final energy level. We are looking for the lowest-energy line or lowest-energy transition to give the photon with the least energy. Therefore, we need the energy level closest to $n = 1$, which is $n = 2$.

B. We can use Equation 2.3.3 to calculate the energy difference between $n = 2$ and $n = 1$.

$$\Delta E = -2.18 \times 10^{-18} J \left(\frac{1}{1^2} - \frac{1}{2^2}\right) = -1.64 \times 10^{-18} J$$

Note that this change in energy is negative because the electron is moving closer to the nucleus and is at a lower energy. This means that a photon of that energy is emitted. The energy of the photon is always a positive value.

C. Since energy is conserved, the change in energy calculated in B must be the energy of the photon emitted. We can rearrange the following equation to calculate the wavelength of the photon that given the energy corresponding to the transition.

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\text{J} \cdot \text{s}) \cdot (3.00 \times 10^{8}\text{m/s})}{1.64 \times 10^{-18}\text{J}} = 1.22 \times 10^{-7} m$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets, producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone.

Exercise 2.3.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n = 5$ orbit. Calculate the wavelength of the *second* line (i.e. the second lowest energy transition to $n = 5$) in the Pfund series.

Answer available at the end of this section.

Example 2.3.2

A hydrogen atom with an electron in its ground state absorbs a photon with a wavelength of 97.2 nm. What energy level is the electron in after the absorption?

Given: wavelength of light absorbed, initial n

Asked for: n value after the transition

Strategy:

A. Since the photon is absorbed, the energy of the final state is greater than the initial state. Calculate the energy of the photon using Equation 2.2.7. This gives the energy difference between the ground state, $n = 1$, and the excited state that we are trying to find.
B. Calculate the energy of the ground state using Equation 2.3.2.
C. Calculate the energy of the excited state using the energies calculated in B and A.
D. Find the n value for the excited state.

Solution:

A. Given the wavelength of the photon, we can calculate the energy of the photon. Ensure that you convert between m and nm, so that the units cancel.

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{Js})\left(\frac{3.00\times10^{8}\text{ m}}{s}\right)}{97.2\text{ nm}}\left(\frac{10^{9}\text{ nm}}{m}\right) = 2.045 \times 10^{-18}\text{ J}$$

B. The electron is initially in the ground state, $n = 1$, so we can calculate the initial energy:

$$E_1 = -2.18 \times 10^{-18} J \left(\frac{1}{1^2}\right) = -2.18 \times 10^{-18} J$$

C. Once the photon is absorbed, the electron moves to higher energy and we can calculate the energy at the new level. Note that the gap between the energy levels is equal to the energy of the photon, i.e. $\text{E}_{\text{photon}} = \Delta\text{E} = 2.05 \times 10^{-18}$ J.

$$\Delta\text{E} = E_n - E_1$$

$$E_n = -2.18 \times 10^{-18}\ \text{J} + 2.045 \times 10^{-18}\ \text{J} = -1.3 \times 10^{-19}\ \text{J}$$

D. To find the energy level, i.e. the n-value, we will again use Equation 2.3.2:

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{n^2}\right) = -1.349 \times 10^{-19}\ \text{J}$$

$$\text{n}^2 = 16.1$$

$$n = 4$$

Limitations of Bohr's Model

Bohr's model of the atom successfully explained the hydrogen spectrum, but it had limitations.

Successes of Bohr's Model:

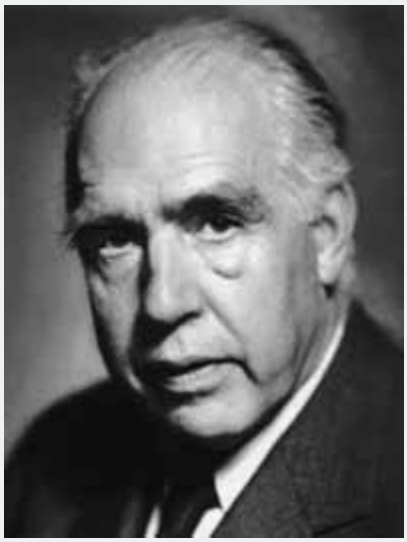
- Electron energy levels are quantized (specific values only).
- Electrons have higher energy when farther from the nucleus, which makes sense as negative electrons are attracted to the positive nucleus.
- Spectral lines correspond to specific electronic transitions.

Limitations of Bohr's Model:

- It could not explain why electrons are restricted to particular orbits and why electrons don't simply collide with the nucleus.
- It only worked for hydrogen—it failed for atoms with more than one electron.
- Electrons do not actually move in fixed circular orbits, as later models would show.

Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

Summary

The light emitted or absorbed by an element is directly related to its atomic structure. Unlike a hot object, which produces a continuous spectrum of all wavelengths, atoms of individual elements emit light only at specific wavelengths, creating a line spectrum. Bohr explained the hydrogen line spectrum by proposing that electrons move in orbits around the nucleus with quantized energy levels. When an electron moves from a higher-energy level to a lower-energy level, it emits light with an energy equal to the difference between the two levels. Conversely, when an electron absorbs energy, it moves to a higher energy level, producing an absorption spectrum. This absorption spectrum appears as a continuous spectrum with dark lines in the same positions as the bright lines in the emission spectrum of the same element.

Bohr's model introduced the concept of quantized energy levels, which was a major step in understanding atomic structure. However, it had limitations. It successfully explained hydrogen's spectrum, but it could not account for the spectra of atoms with more than one electron. Additionally, Bohr described electrons as moving in fixed circular orbits, but later discoveries showed that electrons do not follow simple planetary paths. Despite these shortcomings, Bohr's model helped establish the idea that electrons occupy discrete energy levels and that transitions between these levels produce characteristic atomic spectra.

Glossary

absorption spectrum
: The spectrum produced by the emission of light by atoms as an electron moves from a lower energy level to a higher energy level.

emission spectrum
: The spectrum produced by the emission of light by atoms as an electron moves from a higher energy level to a lower energy level.

excited state
: State having an energy greater than the ground-state energy.

ground state
: State in which the electrons in an atom, ion, or molecule have the lowest energy possible.

line spectrum
: The electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise $2.3.1$: The Pfund Series

Lowest energy line is $n = 6$ to $n = 5$, so second lowest energy line is $n = 7$ to $n = 5$.

4.65×10^{-6} m or 4.65×10^{3} nm

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2.4: The Wave-Particle Duality of Matter

Learning Objective

- Extend the concept of wave-particle duality to electrons

Photons of light are individual packets of energy having characteristics of particles. This idea, that energy is concentrated in localized bundles, was a significant departure from the classical view that energy is spread out continuously as a wave. Our modern understanding of electronic structure builds on this concept by recognizing that not only does energy have particle-like properties, but matter also has wave-like properties.

The Wave Character of Electrons

In 1924, a young French physicist, Louis de Broglie (1892–1972; Nobel Prize, 1929), proposed that particles—such as electrons—could exhibit wave-like behaviour. He suggested that an electron could be described by a wave with a wavelength (λ) given by:

$$\lambda = \frac{h}{mu} \tag{2.4.1}$$

where

- h is Planck's constant,
- m is the mass of the particle, and
- u is the velocity of the particle.

Although you are not required to calculate de Broglie wavelengths in CHM 135H, this equation helps illustrate the concept that wavelength is a fundamental property of matter, not just electromagnetic radiation. Unlike the wavelengths discussed earlier in this chapter (which relate to electromagnetic waves), the de Broglie wavelength applies to physical particles and depends on velocity rather than frequency.

de Broglie also sought to explain why only certain orbits were allowed in Bohr's model of the hydrogen atom. While Bohr assumed electrons followed fixed circular orbits, de Broglie suggested that an electron behaves as a standing wave around the nucleus. For the wave to be stable, only whole numbers of wavelengths could fit perfectly into the orbit (Figure $2.4.1$). In this model, the lowest energy level ($n = 1$) corresponds to a wave that forms one complete wavelength around the nucleus. Higher energy levels contain more wavelengths, with nodes—regions where the amplitude is zero—appearing as n increases. As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. While de Broglie's model helped explain why Bohr's quantization worked, it was still incomplete. Later models showed that electrons do not move in fixed circular orbits.

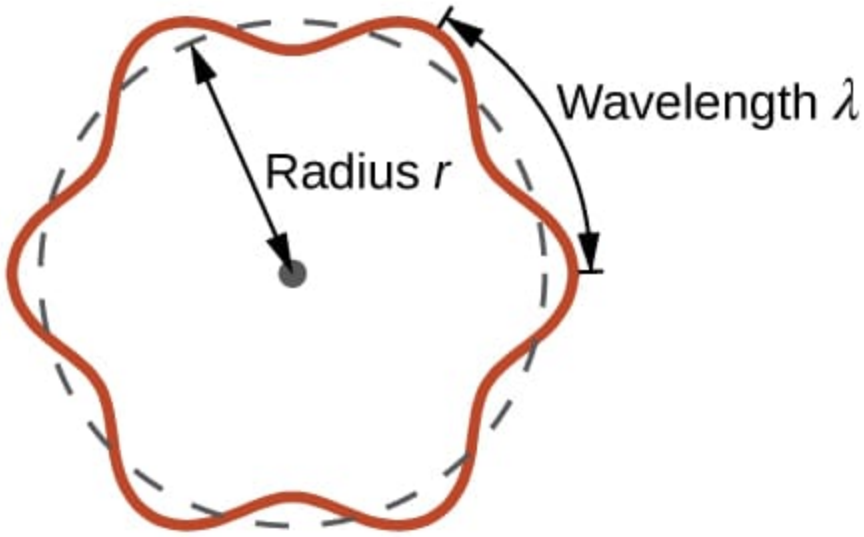


Figure $2.4.1$*: If an electron is viewed as a standing wave around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible. The standing wave shown here corresponds to* $n = 6$ *with six wavelengths around the nucleus.*

Shortly after de Broglie's proposal, C. J. Davisson and L. H. Germer at Bell Laboratories provided experimental evidence for the wave-like nature of electrons. They observed interference patterns when electrons passed through a nickel crystal, a phenomenon typically seen with waves (Figure $2.4.2$). This confirmed that electrons exhibit wavelike behaviour.

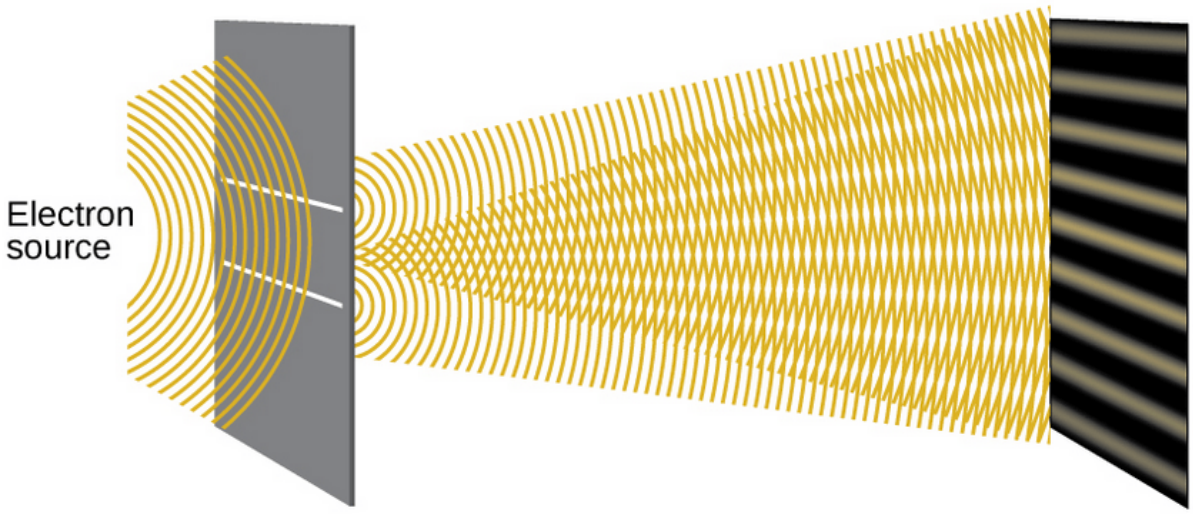
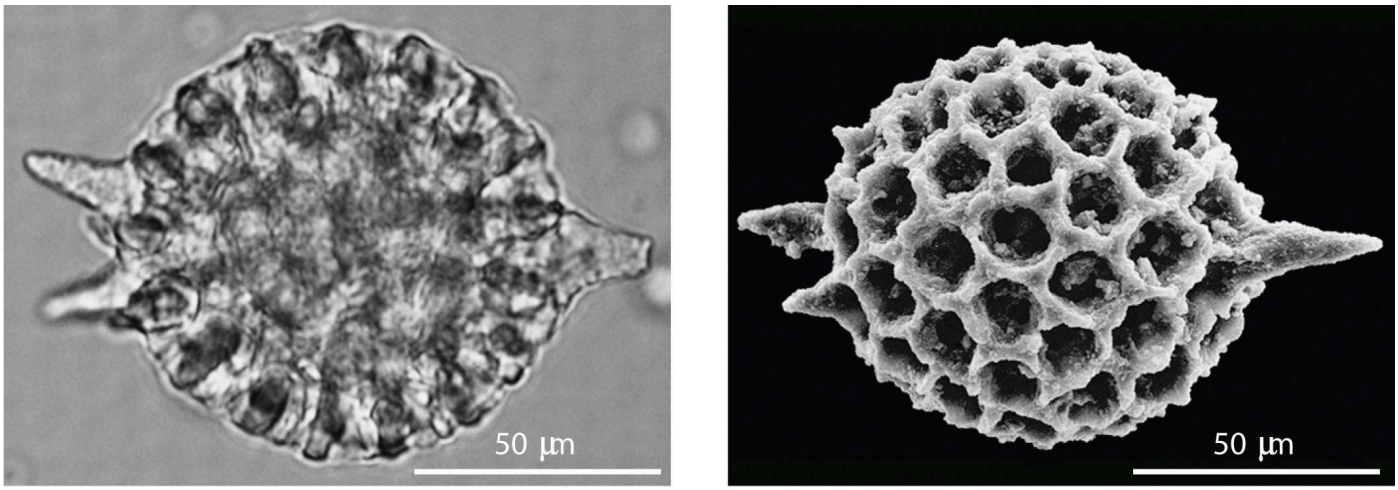


Figure $2.4.2$***:*** *The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior.*

If electrons have wave properties, why hadn't this been observed before? The answer lies in Planck's constant (h), which is an extremely small number. For objects with large masses, such as a baseball or even a neutron, the de Broglie wavelength is so short (smaller than an atomic nucleus) that it is undetectable. However, for very small particles like electrons, the wavelength is significant, meaning they behave as both particles and waves. This principle is applied in electron microscopes, which use the short wavelength of electrons to resolve details far beyond what is possible with visible light (Figure $2.4.3$).



(a) Radiolarian under light microscope **(b) Radiolarian under electron microscope**

Figure 2.4.3: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) can resolve finer details than a light microscope (a). Radiolaria, which are shown here, are unicellular planktonic organisms.

The Heisenberg Uncertainty Principle

Waves do not have a fixed position—they are spread out in space. If electrons behave as waves, it should be difficult to define their exact location at any given moment. This idea was formulated mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932).

Heisenberg's Uncertainty Principle states that:

> There is a fundamental limit to how precisely we can simultaneously know certain pairs of properties of a particle, such as its position and momentum.

For electrons, this means that the more accurately we know their position, the less accurately we can know their velocity (or energy), and vice versa. This uncertainty is not due to flaws in measurement but is an inherent property of quantum systems. Here is a mathematical description of the Heisenberg uncertainty principle if you're interested.

Bohr's model of the hydrogen atom violated Heisenberg's principle by assuming that electrons follow precise circular orbits with both a known radius (position) and energy. Given the wave-like nature of electrons, this is impossible. Modern atomic models replace fixed orbits with probability distributions, where an electron's location is described in terms of likelihood rather than a definite path.

Summary

Electrons exhibit both particle and wave properties, a concept known as wave-particle duality. Louis de Broglie proposed that electrons have wavelengths, helping to explain Bohr's quantized orbits in terms of standing waves. Experimental confirmation came from Davisson and Germer, who showed that electrons create interference patterns just like waves.

However, Bohr's model incorrectly described electrons as moving in fixed circular orbits. The Heisenberg Uncertainty Principle showed that it is impossible to precisely determine both an electron's position and momentum simultaneously.

Glossary

Heisenberg uncertainty principle
: Rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time; the uncertainty principle is a consequence of quantum particles exhibiting wave-particle duality.

node
: Any point of a standing wave with zero amplitude; also regions of an orbital where the probability of finding an electron is zero.

photon
: The smallest possible packet of electromagnetic radiation, a particle of light.

standing wave
: A localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized; also called stationary wave.

wave-particle duality
: Term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency).

Contributors and Attributions

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2.5: The Quantum-Mechanical Model of the Atom

Learning Objectives

- Describe the four quantum numbers from Schrödinger's equation and their allowed values
- Use quantum numbers to describe the energy, shape, size, and orientation of orbitals

The Quantum-Mechanical Model of an Atom

The Heisenberg uncertainty principle and the wave-like nature of electrons made it clear that classical physics could not accurately describe electron motion in atoms. Scientists needed a new approach that accounted for the wave behaviour of electrons.

Shortly after de Broglie proposed that electrons behave as standing waves, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933) developed a mathematical framework to describe them. His Schrödinger equation treated electrons not as tiny particles moving in fixed orbits but as three-dimensional waves.

Schrödinger's equation successfully predicted the energy levels of hydrogen, matching experimental data. However, the wave Schrödinger described—called a wavefunction (ψ, pronounced "psi")—does not represent the physical motion of an electron. Instead, Max Born later proposed that the square of the wavefunction, $|\psi|^2$, represents the probability of finding an electron in a particular region of space. Rather than picturing the electron as a small object moving along a definite path, we can think of it as spread out in a "cloud" of probability around the nucleus. This probability cloud is called an orbital, a three-dimensional region where the electron is most likely to be found.

In mathematical terms, the Schrödinger equation is written as:

$$\hat{H}\psi = E\psi$$

where:

- $\hat{H}$ is the Hamiltonian operator, a set of mathematical operations,
- ψ is the wavefunction, which can be used to find the probability of locating an electron in a given region,
- E is the total energy of the electron.

Schrödinger's work, along with contributions from Heisenberg and others, led to the quantum-mechanical model of the atom.

While the details of the Schrödinger wave equation are beyond the scope of CHM 135H, here are some key findings:

- Solutions to the wave equation are called wavefunctions and are represented by the Greek letter psi, ψ.
- Each wavefunction corresponds to a specific energy level.
- The wavefunction itself has no direct physical meaning regarding electron motion.
- $|\psi|^2$ represents the probability density, showing how likely it is to find the electron at each point in space. Regions where $|\psi|^2$ is relatively large are those where the electron is most likely to be found.
- These high probability regions are called orbitals.
- Each orbital is defined by three quantum numbers, which describe its size, shape, and orientation.
- The allowed values of these quantum numbers come from the mathematical solutions of Schrödinger's equation.

Quantum Numbers

Solving Schrödinger's equation for the hydrogen atom results in three quantum numbers, which define the properties of each orbital.

The Principal Quantum Number (*n*)

The principal quantum number, n, determines the size and energy of an orbital:

$$n = 1, 2, 3, 4, \ldots$$

- As n increases, the electron is, on average, farther from the nucleus and has higher energy.
- Electrons with higher n values are less tightly bound to the nucleus and are easier to remove.
- All orbitals with the same n value make up a principal shell.
- n is a positive integer and we will see that it corresponds to the n value in Equation 2.2.2 (from the Bohr model).

The Angular Momentum Quantum Number (*l*)

The angular momentum quantum number, l, determines the shape of an orbital. The allowed values of l depend on l and range from 0 to n–1:

$$l = 0, 1, 2, \ldots, n-1$$

- For example, for $n = 1$, the only allowed value is $l = 0$ and for $n = 2$, the allowed values are $l = 0$ or $l = 1$.
- Orbitals with the same n and l values belong to the same subshell. Subshells have different shapes but the same energy.

The Magnetic Quantum Number (m_l)

The magnetic quantum number, m_l, describes the orientation of an orbital in space. The allowed values of m_l depend on p:

$$m_l = -l, (-l+1), \ldots, 0, \ldots, (l-1), l$$

- If \(l = 0\), the only allowed value for m_l is 0 (one possible orientation).
- If \(l = 1\), the allowed values of m_l are –1, 0, +1 (three possible orientations).
- If \(l = 2\), the allowed values of m_l are –2, –1, 0 , +1, +2 (five possible orientations).

Each unique combination of n, l, and m_l describes a specific atomic orbital.

Example 2.5.1: Working with shells and sub-shells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the \(n = 4\) shell of an atom

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given \(n = 4\), calculate the allowed values of l. From these allowed values, count the number of subshells.
B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to n – 1. If \(n = 4\), then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For \(l = 0\), m_l can be only 0, and thus the \(l = 0\) subshell has only one orbital. For \(l = 1\), m_l can be 0 or ±1; thus the \(l = 1\) subshell has three orbitals. For \(l = 2\), m_l can be 0, ±1, or ±2, so there are five orbitals in the \(l = 2\) subshell. The last allowed value of l is \(l = 3\), for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the \(l = 3\) subshell. The total number of orbitals in the \(n = 4\) principal shell is the sum of the number of orbitals in each subshell and is equal to 16.

Exercise 2.5.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with \(n = 3\)?

Answer available at the end of this section.

Rather than listing quantum numbers each time, chemists use a letter notation to represent different subshells. The angular momentum quantum number (l) determines the type of subshell and is assigned a specific letter:

l =	0	1	2	3
Designation	s	p	d	f

The principal quantum number (n) is written before the letter. For example:

1s orbital → \(n = 1\), \(l = 0\)
2p subshell → \(n = 2\), \(l = 1\) (contains three $2p$ orbitals: m_l = –1, 0, +1)
3d subshell → \(n = 3\), \(l = 2\) (contains five $3d$ orbitals: m_l =–2, –1, 0, +1, +2)

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 2.4.1):

Each principal shell (n) contains n subshells:

For \(n = 1\), there is only one subshell ($1s$).
For \(n = 2\), there are two subshells ($2s$, $2p$).
For \(n = 3\), there are three subshells ($3s$, $3p$, $3d$).

Each subshell contains a specific number of orbitals, based on the possible m_l values:

The s subshell ($l = 0$) has 1 orbital.
The p subshell ($l = 1$) has 3 orbitals.
The d subshell ($l = 2$) has 5 orbitals.
The f subshell ($l = 3$) has 7 orbitals.

Table 2.5.1: Values of n, l, and m_l through $n = 4$

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	$1s$	0	1	1
2	0	$2s$	0	1	4
	1	$2p$	–1, 0, 1	3	
3	0	$3s$	0	1	9
	1	$3p$	–1, 0, 1	3	
	2	$3d$	–2, –1, 0, 1, 2	5	
4	0	$4s$	0	1	16

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
	1	$4p$	–1, 0, 1	3	
	2	$4d$	–2, –1, 0, 1, 2	5	
	3	$4f$	–3, –2, –1, 0, 1, 2, 3	7	

You don't need to memorize this table. Instead, you should be able to recreate it by applying the rules for quantum numbers based on the Schrödinger equation.

Exercise 2.5.2

Identify the subshell in which electrons with the following quantum numbers are found: \(*n* = 3\), \(*l* = 1\).

Answer available at the end of this section.

The Spin Quantum Number

While the three quantum numbers n, l, and m_l define atomic orbitals—regions of space where an electron is most likely found—the spin quantum number (m_s) describes an electron's spin. This property determines how electrons occupy orbitals.

An electron can only have one of two possible spin values:

$$m_s = +\frac{1}{2}\ (\text{spin up}) \qquad \text{or} \qquad m_s = -\frac{1}{2}\ (\text{spin down})$$

These values are quantized, meaning an electron can only spin in these two specific ways.

As shown in Figure 2.5.1, you can think of an electron as a tiny magnet. A spinning electron (or any moving charged particle) generates a magnetic field by its motion, which is why the terms "spin up" and "spin down" are used.

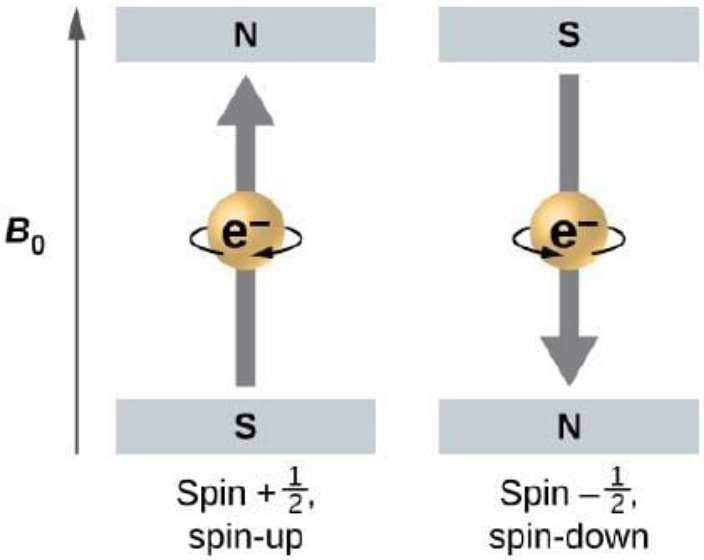


Figure 2.5.1: *Electrons with spin values \(±\ce{1/2}\) in an external magnetic field.*

Each atomic orbital can hold two electrons, but they must have opposite spins (one with spin up, $m_s = \frac{1}{2}$, and one with spin down, $m_s = -\frac{1}{2}$).

Example 2.5.2

Calculate the maximum number of electrons that can occupy a shell with \(*n* = 5\). Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Given: value of n

Asked for: maximum number of electrons in that shell

Strategy:

A. Given \(*n* = 5\), calculate the allowed values of l.
B. For each allowed value of l, find the allowed values of m_l.
C. Consider the m_s values allowed for each orbital

Solution:

A. $n = 5$, so l can have values of 0, 1, 2, 3, 4

B. For \(*l* = 0\), \(*m_l* = 0\): 1 orbital

For \(l = 1\), \(*m_l* = -1, 0, 1\): 3 orbitals

For \(*l* = 2\), \(*m_l* = -2, -1, 0, 1, 2\): 5 orbitals

For \(*l* = 3\), \(*m_l* = -3, -2, -1, 0, 1, 2, 3\): 7 orbitals

For \(*l* = 4\), \(*m_l* = -4, -3, -2, -1, 0, 1, 2, 3, 4\): 9 orbitals

C. Each of the 25 orbitals in B could contain an electron with m_s = 1/2 or -1/2, so the maximum electrons in $n = 5$ is 50.

Exercise 2.5.3

Calculate the maximum number of electrons that can occupy a shell with \(*n* = 2\). Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Answer available at the end of this section.

Shapes of Atomic Orbitals

Orbitals represent regions of space where electrons are most likely to be found. These regions are determined mathematically from Schrödinger's equation and have different shapes and probabilities of containing an electron. We will start our discussion with the s-orbital (\(*l* = 0\)) and continue from there.

s Orbitals

One way to visualize electron probability distributions is shown in Figure 2.5.2 for the 1s orbital of hydrogen. The function Ψ^2 describes the probability density, the likelihood of finding an electron at a given distance r from the nucleus. The 1s orbital is spherically symmetrical, meaning the probability of finding a 1s electron at any given point depends only on its distance from the nucleus. The probability density is greatest at \(*r* = 0\) (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is very small but not zero.

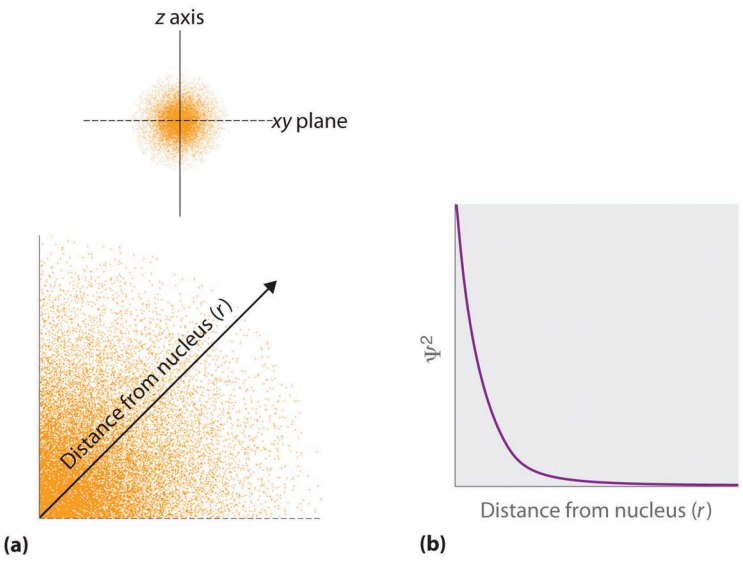


Figure 2.5.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at \(r = 0\) (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but *not* zero.

A different way to analyze electron position is by calculating radial probability—the probability of finding an electron at a specific distance, r, from the nucleus. This is done by adding up all the electron probabilities within a thin spherical shell at that distance, similar to the layers of an onion (part (a) in Figure 2.5.3). Although probability density is highest at $r = 0$, the total probability of finding an electron near the nucleus is low because the surface area of small shells is tiny. The surface area of spherical shells increases rapidly as r increases (part c), following the formula $4\pi r^2$. Because of this, the radial probability has a peak at a certain distance from the nucleus (part d).

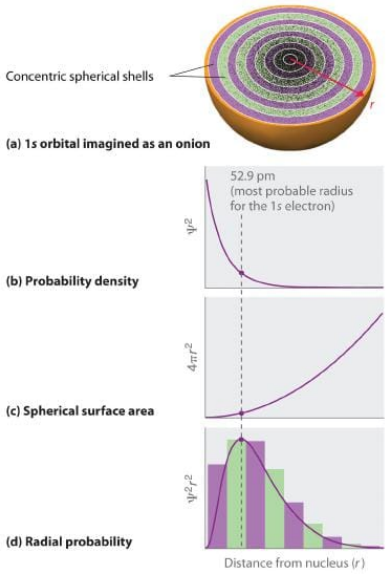


Figure 2.5.3 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus \(r\) shows that the electron probability density is greatest at \(r = 0\) and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the *radial probability*) shows a peak.

For hydrogen, this peak occurs at 0.529 Å (52.9 pm)—the same as the electron's orbit in Bohr's model. However, in Bohr's model,

the electron was always at this distance, whereas in Schrödinger's model, it is only at this distance some of the time due to its wave-like nature and the Heisenberg uncertainty principle.

Figure 2.5.4 compares the radial probability densities for the hydrogen 1s, 2s, and 3s orbitals. All s orbitals are spherically symmetrical. In the 2s and 3s orbitals, the radial probability does not decrease smoothly with distance. Instead, there are alternating regions of high and zero probability. These regions of zero electron probability are called spherical nodes, where the electron cannot be found.

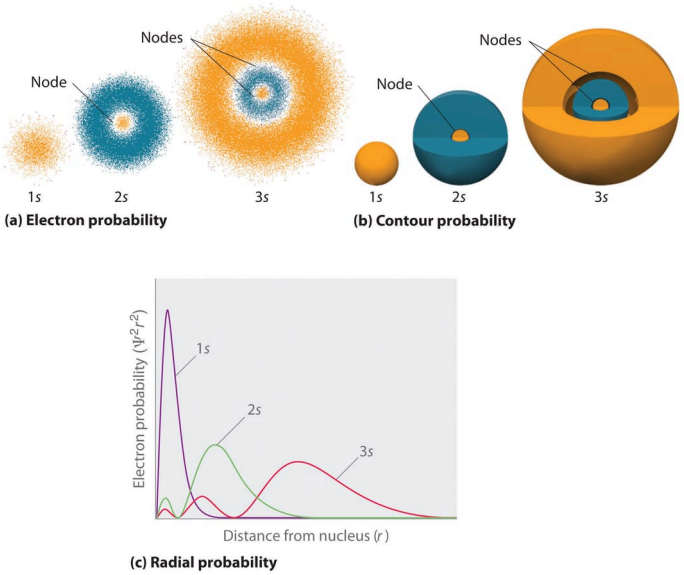


Figure 2.5.4 : Probability Densities for the 1s, 2s, and 3s Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. (c) In these plots of radial probability, the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of *r*.

Three things happen to s orbitals as n increases (Figure 2.5.4):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes (points with zero amplitude.)
3. For a given atom, the s orbitals also become higher in energy as n increases because of their increased distance from the nucleus.

Orbitals are often drawn as three-dimensional surfaces that enclose about 90% of the electron density, as shown for the hydrogen 1s, 2s, and 3s orbitals in part (b) in Figure 2.5.4. While these surfaces show the overall size of the orbitals, they do not normally show the internal spherical nodes (because those nodes lie inside the 90% boundary). For most chemical bonding discussions, the exact positions of these spherical nodes are not crucial.

p Orbitals

Unlike s orbitals, p orbitals are not spherically symmetrical. Because the 2p subshell has \(l = 1\), with three values of m_l (–1, 0, and +1), there are three 2p orbitals.

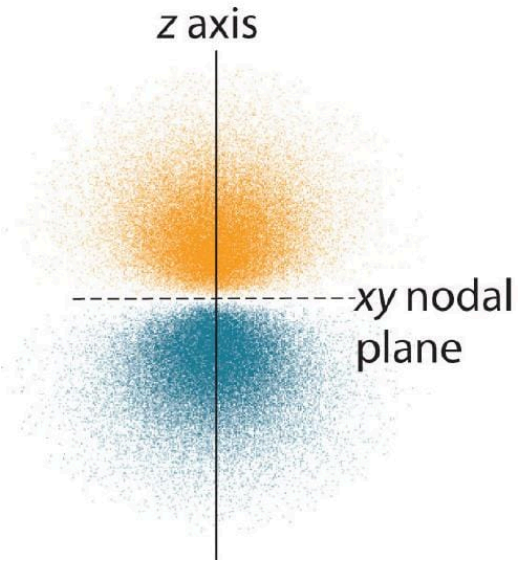


Figure 2.5.5, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 2.5.5. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 2.5.6, the other two $2p$ orbitals have identical shapes, but they lie along the *x* axis (2 p_x) and *y* axis ($2p_y$), respectively. Note that each p orbital has just one nodal plane. In each case, the phase of the wave function for each of the $2p$ orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

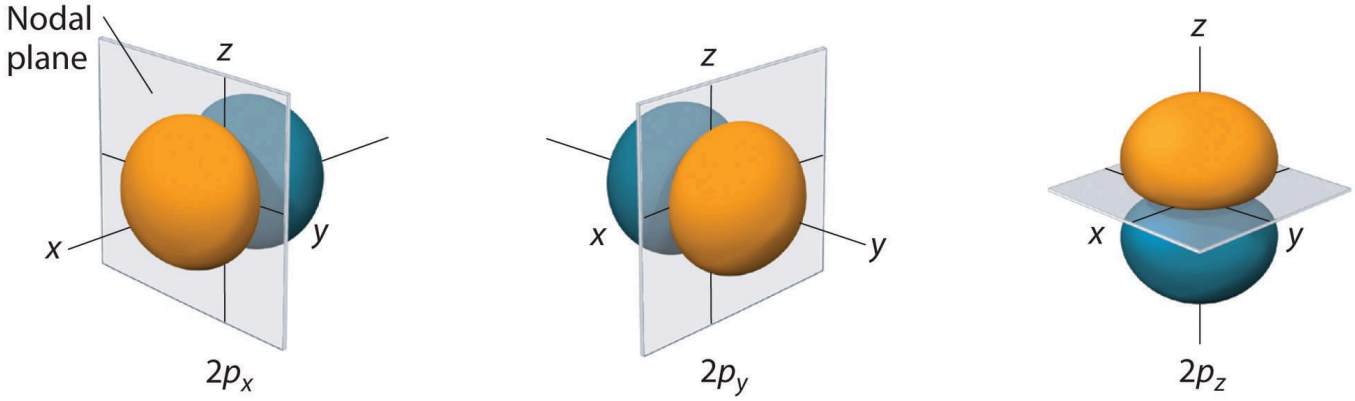


Figure 2.5.6 The Three Equivalent $2p$ Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each $2p$ orbital.

Just as with the s orbitals, the size and complexity of the p orbitals for any atom increase as the principal quantum number n increases. The shapes of the 90% probability surfaces of the $3p$, $4p$, and higher-energy p orbitals are, however, essentially the same as those shown in Figure 2.5.6 .

Figure 2.5.7 shows the radial probability function of the $1s$, $2s$, and $2p$ orbitals. From these plots, we can see that the probability peak of the 1s orbital is closest to the nucleus; thus it is the most penetrating with the electron spending more of its time closer to the nucleus, while the $2s$ and $2p$ have their peak in probability at a farther distance from the nucleus. This makes sense as we know the $1s$ orbital is lower in energy than the $2s$ and $2p$ orbitals (remember the electron is negative and so is attracted to the positive nucleus). The $2s$ orbital and the $2p$ orbital have different radial probability functions, but interestingly on average an electron in either of these orbitals experiences a similar attraction to the nucleus. The $2p$ orbital has its maximum probability

closer to the nucleus but the $2s$ orbital has a small central lobe that penetrates closer to the nucleus within the space occupied by the $1s$ orbital. The relevance of these details will become clear when discussing the energy of the various orbitals.

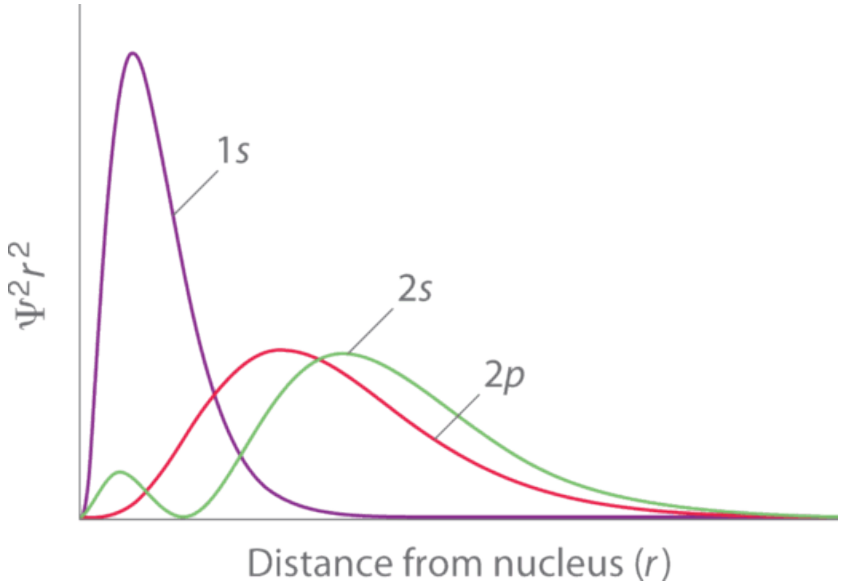


Figure $2.5.7$: Orbital Penetration. A comparison of the radial probability distribution of the $2s$ and $2p$ orbitals of the hydrogen atom shows that the $2s$ orbital penetrates inside the 1s orbital more than the $2p$ orbital does. (CC-BY-NC-SA, LibreText)

d Orbitals

Subshells with \(l = 2\) have five d orbitals; the first principal shell to have a d subshell corresponds to \(n = 3\). The five d orbitals have m_l values of –2, –1, 0, +1, and +2.

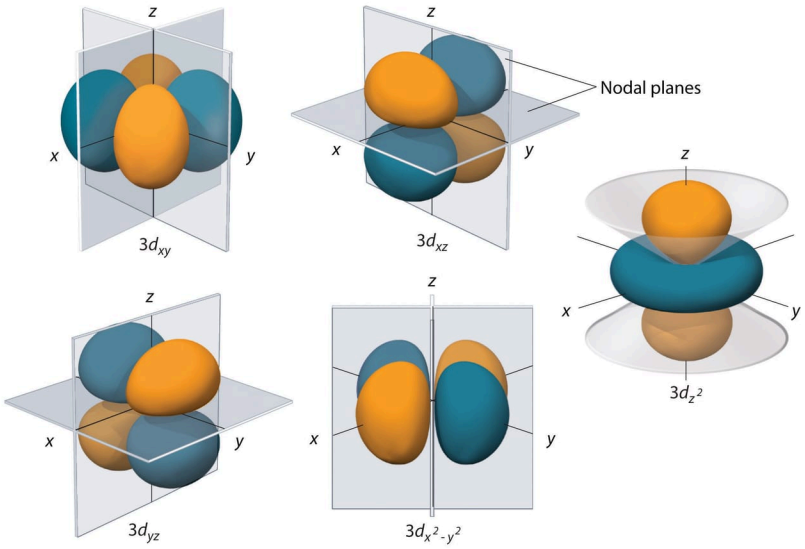


Figure $2.5.8$: The Five Equivalent $3d$ Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen $3d$ orbitals. Four of the five $3d$ orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth $3d$ orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others.

The hydrogen 3d orbitals, shown in Figure $2.5.8$, have more complex shapes than the $2p$ orbitals. All five $3d$ orbitals contain two nodal surfaces. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure $2.5.8$.

f Orbitals

Principal shells with \(*n* = 4\) can have subshells with \(*l* = 3\) and m_l values of –3, –2, –1, 0, +1, +2, and +3. These subshells consist of seven f orbitals. Each f orbital has three nodal surfaces, so their shapes are complex. We will not discuss f-orbitals further in CHM 135H, and orbitals with higher values of l will not be discussed in this course.

Orbital Energies in the Hydrogen Atom

So far, we have discussed the shapes of atomic orbitals, but now we consider their relative energies.

For a hydrogen atom with a single electron, Schrödinger's equation predicts the same energy levels as Bohr's model, which match experimental atomic emission spectra. Electrons can only occupy specific energy levels, and they cannot exist between them. The energy of an electron in an atom is therefore quantized, meaning it can only take certain allowed values. While electrons can move between levels by absorbing or emitting energy, they cannot stay between levels.

Figure $2.5.9$ shows the relative energies of orbitals for $n \leq 4$ in a hydrogen atom. In hydrogen, the orbital energy depends only on the principal quantum number n, so the $2s$ and $2p$ orbitals have the same energy, as do the $3s$, $3p$, and $3d$ orbitals. These orbitals are degenerate, meaning they have the same energy. This is consistent with the discussion surrounding Figure $2.5.7$ above that compared the radial probability distributions for the $1s$, $2s$ and $2p$ orbitals. In the 1s orbital the electron spends more time closer to the nucleus and so this is a lower energy state compared to the $2s$ and $2p$ orbitals. The $2s$ and $2p$ orbitals have different probability distributions but on average an electron in either of these orbitals experiences the same attraction to the nucleus and so both orbitals exist at the same energy level. The situation is more complex in multi-electron atoms, something we will explore in the next section.

Unlike Bohr's model, which predicted only one orbit per energy level, quantum mechanics shows that for each principal quantum number n, there are multiple orbitals with different shapes and orientations. The \(*n* = 2\) shell contains four orbitals (one $2s$ and three $2p$), the \(*n* = 3\) shell contains nine orbitals, and the \(*n* = 4\) shell contains sixteen orbitals. The energy levels get closer together as n increases, following this equation:

$$E_n = -2.18 \times 10^{-18} \left(\frac{1}{n^2} \right)$$



Figure $2.5.9$: Orbital Energy Level Diagram for the Hydrogen Atom. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.

The most stable orbitals, or those with the lowest energy, are closest to the nucleus. In its ground state, a hydrogen atom's single electron is in the $1s$ orbital. If the atom absorbs energy, the electron moves to a higher-energy orbital, such as one of the $n = 2$ orbitals. This is called an excited state.

Summary

The quantum mechanical model describes the electron's position probabilistically using a mathematical function called a wavefunction (Ψ). The squared magnitude of the wavefunction, Ψ^2, represents the probability density, or the likelihood of finding an electron in a given region. Atomic orbitals describe areas where electrons are most likely to be found, and each orbital has a specific energy.

An atomic orbital is defined by three quantum numbers. The principal quantum number (n) determines the orbital's size and energy. The angular momentum quantum number (l) describes its shape, and orbitals with the same n and l belong to the same subshell. The magnetic quantum number (m_l) determines the orbital's orientation in space. In addition, each electron has a spin quantum number (m_s), which can be +1/2 or –1/2.

The four main types of orbitals correspond to different values of l. s orbitals (\(l = 0\)) are spherical. p orbitals (\(l = 1\)) have a dumbbell shape and contain a nodal plane through the nucleus. f orbitals (\(l = 2\)) have more complex shapes with two nodal surfaces, and f orbitals (\(l = 3\)) are even more complex.

For a hydrogen atom or any ion with a single electron, all orbitals with the same n have the same energy. For the hydrogen atom, the energy can be calculated by the principal quantum number alone using this equation.

$$E_n = -2.18 \times 10^{-18} \left(\frac{1}{n^2} \right)$$

As n increases, the orbitals become larger and higher in energy. An atom is in its ground state when its electrons occupy the lowest-energy orbitals, and it is in an excited state when one or more electrons move to higher-energy orbitals.

Glossary

angular momentum quantum number (*l*)
: Quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum.

atomic orbital
: A region of space where an electron is most likely found, described by quantum numbers.

***d* orbital**
: A region of space with high electron density that is either four-lobed or contains a dumbbell and torus shape; describes orbitals with \(l = 2\); an electron in this orbital is called a *d* electron.

electron density
: A measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ.

***f* orbital**
: A multilobed region of space with high electron density, describes orbitals with \(l = 3\); an electron in this orbital is called an *f* electron.

magnetic quantum number (m_l)
: Quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field.

***p* orbital**
: A dumbbell-shaped region of space with high electron density, describes orbitals with \(l = 1\); an electron in this orbital is called a p electron.

principal quantum number (*n*)
: Quantum number specifying the shell an electron occupies in an atom.

quantum mechanical model
: Schrödinger's model of the atom treating electrons as three-dimensional waves spread out in a probability cloud

(orbital) around the nucleus.

radial probability
The probability of finding an electron at a specific distance, r, from the nucleus.

s orbital
A spherical region of space with high electron density, describes orbitals with \(l = 0\); an electron in this orbital is called an s electron.

Schrödinger equation
A mathematical framework developed by Erwin Schrödinger that describes the wave-like behavior of electrons; this equation can predict the energy levels of hydrogen, resulting in quantum numbers that define the properties of hydrogen orbitals.

shell
A set of orbitals with the same principal quantum number, n.

spin quantum number (m_s)
Quantum number specifying the electron spin direction, either +1/2 or -1/2.

subshell
A set of orbitals in an atom with the same values of n and l.

wavefunction (ψ)
A mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum.

Answers

Exercise 2.5.1**: n=3 Shell Structure**
three subshells; nine orbitals

Exercise 2.5.2
3p

Exercise 2.5.3
8 electrons

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2.6: Characteristics of Many-Electron Atoms

Learning Objectives

- Describe how electron shielding and penetration affect the energy of subshells
- Contrast the orbital energy levels in the hydrogen atom to the energy levels in polyelectronic atoms.

The quantum mechanical model successfully describes the energies of hydrogen atomic orbitals, but extending this model to multi-electron atoms is more complex. Schrödinger's equation cannot be solved exactly for atoms with more than one electron due to electron-electron interactions. However, approximate solutions help us understand electron configurations. Before exploring electron configurations, we need to introduce the Pauli exclusion principle, shielding, and penetration.

The Pauli Exclusion Principle

Austrian physicist Wolfgang Pauli (1900–1958) determined that no two electrons in an atom can have the same four quantum numbers (n, l , m_l, m_s). This is known as the Pauli exclusion principle.

Since an orbital is defined by the quantum numbers n, l , m_l, each orbital can hold a maximum of two electrons, one with spin up (m_s = +1/2) and one with spin down (m_s = –1/2). With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

Example 2.6.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2p orbital and predict the maximum number of electrons the 2*p* subshell can accommodate.

Given: orbital is 2p

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to a 2*p* orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2*p* subshell can accommodate.

Solution:

A For a 2*p* orbital, we know that n = 2, l = 1. m_l = –l, (–l +1),..., (l – 1), l, so -1, 0 or 1. There are three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, –1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and –½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, –½), (2, 1, 0, +½), (2, 1, 0, –½), (2, 1, –1, +½), and (2, 1, –1, –½).

C Hence the 2*p* subshell, which consists of three 2*p* orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise 2.6.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer available at the end of this section.

Electron Shielding and Penetration

For a single-electron atom or ion, the energy depends only on the electrostatic attraction between the nucleus and the electron. In multi-electron atoms, however, the total energy also depends on electron-electron repulsions. Because electrons have negative charges, they repel each other, altering orbital energies in ways that must be considered.

One key effect in multi-electron atoms is electron shielding. If an electron is far from the nucleus, most of the inner electrons will be between it and the nucleus. These inner electrons partially cancel the positive charge of the nucleus, reducing the attraction felt by the outer electron. The resulting charge that the outer electron actually experiences is called the effective nuclear charge (Z_{eff}), which is less than the actual nuclear charge (Z). If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of the other electrons present.

Another important concept is penetration, which describes how close an electron in a given subshell can get to the nucleus. The closer an electron can approach the nucleus, the less shielding it experiences and the higher its effective nuclear charge.

The penetration of individual orbitals can be visualized using the radial probability functions. For example, Figure 2.6.1 below shows plots of the radial probability function of the 1s, 2s, and 2p orbitals. From these plots, we can see that the 1s orbital can approach closest to the nucleus and therefore is the most penetrating. While the 2s and 2p have most of their probability at a farther distance from the nucleus (compared to 1s), the 2s orbital and the 2p orbital have different extents of penetration. The 2s orbital can penetrate the 1s orbital because of the small maxima close to the nucleus. The 2p orbital penetrates somewhat into the 1s, but it cannot approach the nucleus as closely as the 2s orbital can. The effect of this penetration is that the 2s orbital is less shielded than the 2p by the 1s electrons and therefore the 2s electrons experience a higher effective nuclear charge than the 2p electrons. Because of this, the 2s sublevel is lower in energy than the 2p sublevel in a multi-electron system.

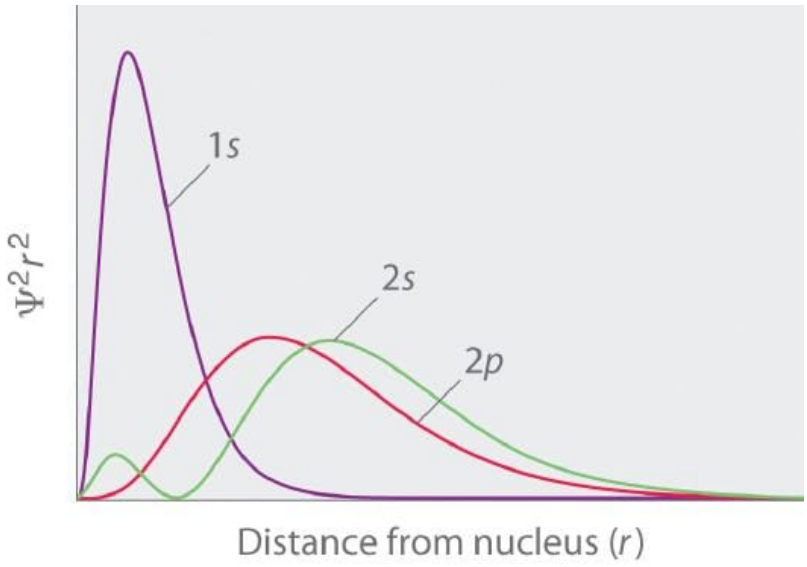


Figure 2.6.1: Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1s orbital more than the 2*p* orbital does. The 2s sublevel experiences a higher effective nuclear charge (less shielding) which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital.

Due to the effects of penetration and shielding, orbitals with the same value of *n* but different values of *l* are not degenerate in a multi-electron atom. For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

Within the same shell value (*n*), the penetrating power of an electron follows this trend in subshells (m_l):

penetration: s > p > d > f

Therefore for a given value of *n*, orbitals with a lower value of l have a lower orbital energy.

orbital energy: s < p < d < f

Orbital Energies in a Multi-electron System

Unlike atoms with only one electron (such as the hydrogen atom), in multi-electron atoms, the values of quantum numbers *n* and *l* both determine the energy of an orbital. The energies of the different orbitals for a typical multi-electron atom are shown in Figure 2.6.2. Within a given principal shell of a multi-electron atom, the orbital energies increase with increasing *l*. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital.

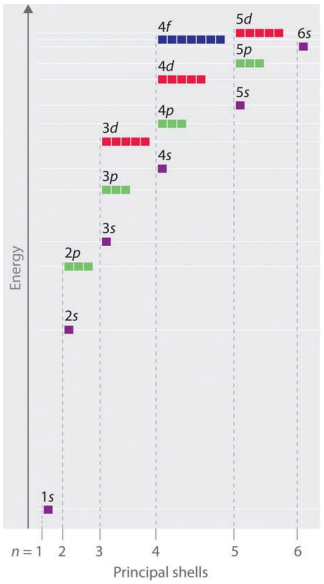


Figure 2.6.2: Orbital Energy Level Diagram for a Typical Multi-electron Atom

Notice in Figure 2.6.2 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

Summary

The Pauli exclusion principle states that no orbital can contain more than two electrons with opposite spins, and no two electrons in the same atom can have the same four quantum numbers.

In multi-electron atoms, electron-electron repulsions complicate energy calculations, but we can approximate their effects using electron shielding and penetration. Shielding occurs when inner electrons partially block the nuclear charge from outer electrons, reducing the effective nuclear charge (Z_{eff}). Penetration describes how effectively an electron gets close to the nucleus. Because of shielding and penetration, orbitals with the same *n* but different *l* values are not degenerate in multi-electron atoms. The energy of orbitals generally follows this trend:s < p < d < f.

This ordering explains why some subshells with higher *n* values (such as 4s) can be lower in energy than subshells with lower n values (such as 3d).

Glossary

effective nuclear charge (Z_{eff})
: Charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding.

electron shielding
: Occurs when inner electrons partially block the nuclear charge from outer electrons, reducing the effective nuclear charge (Z_{eff}).

Pauli exclusion principle
: Principle that specifies that no two electrons in an atom can have the same value for all four quantum numbers..

penetration
: The extent to which an electron in a subshell can approach the nucleus.

Answers

Exercise 2.6.1

(6, 0, 0, +½), (6, 0, 0, –½); two electrons

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2.7: Electronic Configurations

Learning Objectives

- To assign ground state electron configurations to atoms

The ground-state electron configuration of an element represents the lowest-energy arrangement of its electrons in atomic orbitals. Understanding electron configurations allows us to predict and explain many chemical properties of elements.

The Aufbau Principle

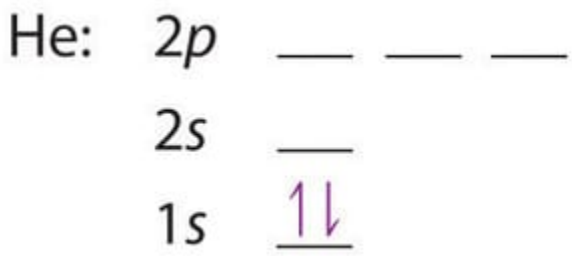
The Aufbau principle (from German, meaning "building up") states that electrons fill orbitals from lowest to highest energy, following a specific order. To determine an element's electron configuration, we:

- Identify the number of electrons in the atom.
- Fill the lowest-energy orbital available without violating the Pauli exclusion principle (no two electrons in an atom can have the same four quantum numbers).

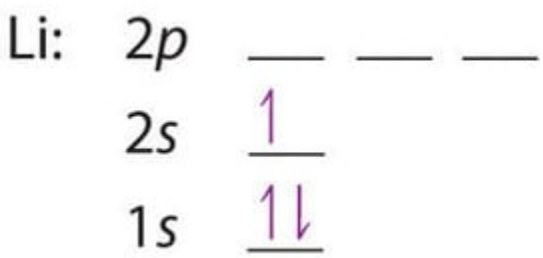
Each orbital holds a maximum of two electrons, one with spin up ↑ (m_s = +1/2) and one with spin down ↓ (m_s = –1/2). A filled orbital is represented as ↑↓, with paired electron spins.

For example, in a hydrogen atom (Z = 1, where Z is the number of protons in the atom), the single electron occupies the 1s orbital, which is the lowest in energy. The electron configuration is written as $1s^1$, read as "one-s-one."

A helium atom (Z = 2) has two electrons. According to the Pauli principle, both electrons can occupy the 1s orbital, but with opposite spins (↑↓). The electron configuration is $1s^2$, where the superscript 2 indicates that the orbital is filled. The orbital diagram for the helium atom is:

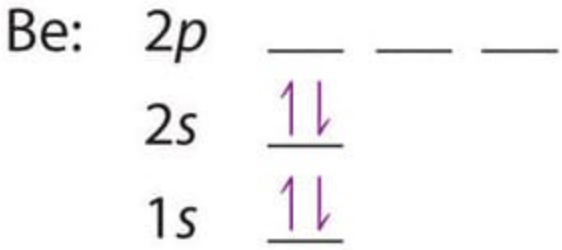


For lithium, (Z = 3), the first two electrons fill the 1s orbital and the third electron is in the next lowest-energy orbital (Figure 2.5.2) 2s. The orbital diagram for lithium is:

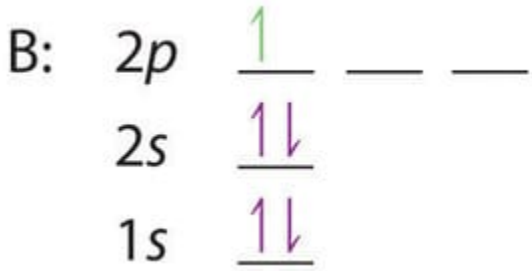


This electron configuration is written as $1s^2 2s^1$.

For beryllium (Z = 4), both the 1s and 2s orbitals are filled: $1s^2 2s^2$.



For boron (Z = 5), the fifth electron must enter the 2p subshell, which contains three degenerate orbitals ($2p_x$, $2p_y$, $2p_z$). Since these orbitals have equal energy, it does not matter which one the electron enters. The electron configuration is $1s^2 2s^2 2p^1$:



Boron has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and one electron in the 2 p orbital.

For carbon (Z = 6), the sixth electron must also go into the 2p subshell. At this point, we have a choice (Figure 2.7.1) :

a) Pair the electron with the existing electron in a 2p orbital.
b) Place it in an empty 2p orbital with opposite spin to the previous electron.
c) Place it in an empty 2p orbital with same spin as previous electron.

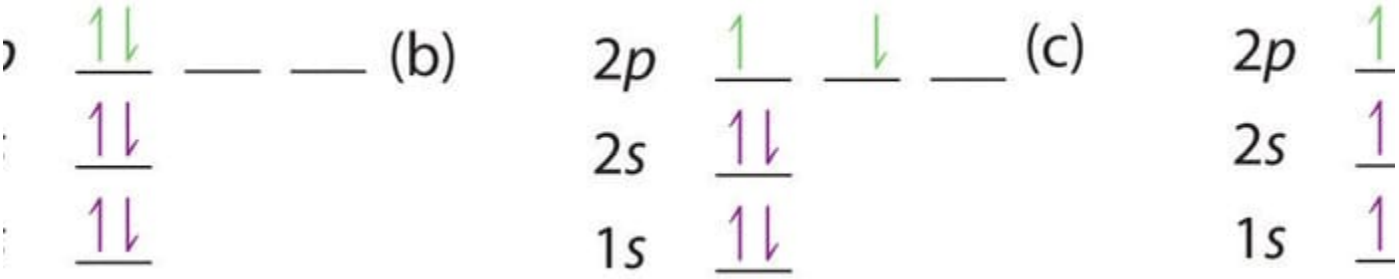
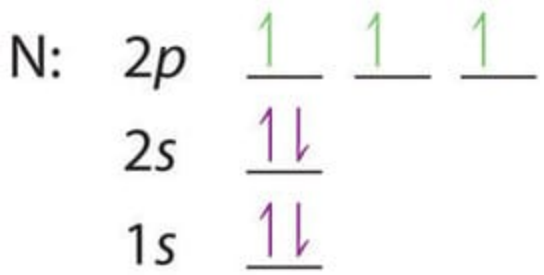


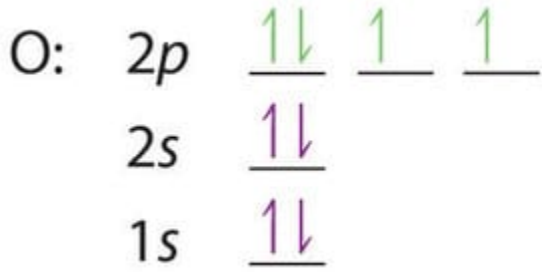
Figure 2.7.1: Three possible electron configurations for carbon, a) paired with the lone electron in the 2 p orbital, b) unpaired with the lone electron and pointing downward, and c) unpaired with the lone electron

Because of electron-electron interactions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice (a). Similarly, experiments have shown that choice (b) is slightly higher in energy (less stable) than choice (c) because electrons in degenerate orbitals tend to line up with their spins parallel; thus, we can eliminate choice (b). The electron configuration in (c) illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which states that the lower energy configuration of an atom is the in where every orbital in a subshell is singly occupied before any orbital is doubly occupied and all of the electrons in singly occupied orbitals have the same spin. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

For nitrogen (Z = 7), the next electron also enters a 2p orbital. Following Hund's rule, since all three 2p orbitals are now occupied by one electron each, nitrogen's configuration is $1s^2 2s^2 2p^3$ with three unpaired electrons.

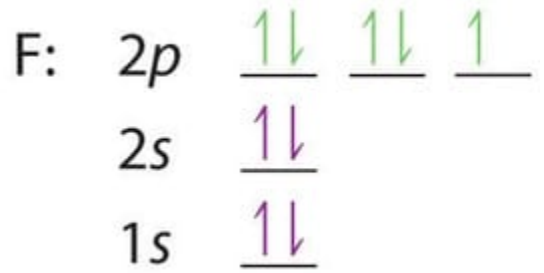


For oxygen (Z = 8), the eighth electron must pair with one of the electrons already in a 2p orbital, giving the configuration $1s^2 2s^2 2p^4$. This results in two unpaired electrons. Because all the *2p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.



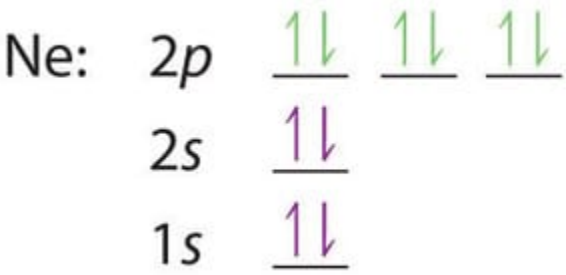
Oxygen has one electron pair in the 1 s orbital, one electron pair in the 2 s pair, and one electron pair, and 2 unpaired electrons in the 2 p orbitals.

For fluorine (Z = 9), another electron is added to a 2p orbital, making the configuration $1s^2 2s^2 2p^5$. At this point, only one 2p orbital contains an unpaired electron:



Fluorine has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 2 electrons pairs with one unpaired electron in the 2 p orbital.

For neon (Z = 10) the last 2p orbital is filled, giving a $1s^2 2s^2 2p^6$ electron configuration:



Neon has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 3 electron pairs in the 2 p orbital.

Elements with completely filled orbitals, such as helium ($1s^2$) and neon ($1s^2 2s^2 2p^6$), are chemically stable. Their electron configurations make them unreactive compared to elements with partially filled orbitals, which are more likely to form chemical bonds.

Valence Electrons

Writing out the full electron configurations for larger atoms can be tedious, so chemists use a shorthand notation. Instead of writing the entire configuration, we use noble gas notation, where the electron configuration of the previous noble gas is represented by its symbol in brackets. Since noble gases have completely filled electron shells, this notation highlights only the valence electrons—the electrons in the outermost shell that are most important in chemical reactions.

For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon (Z = 10), so the electron configuration of sodium, with Z = 11, which is $1s^2 2s^2 2p^6 3s^1$, can be written as $[Ne]3s^1$.

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the **valence electrons**. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium (Na) and lithium (Li), we have:

Na: $1s^2 2s^2 2p^6 3s^1 = [Ne]3s^1$

Li: $1s^2 2s^1 = [He]2s^1$

Both have a single valence electron in an s orbital, which explains why their chemical properties are similar.

Example 2.7.1: Electronic Configuration of Phosphorus

What is its valence electron configuration of phosphorus, Z = 15?

Given: atomic number

Asked for: valence electron configuration for phosphorus

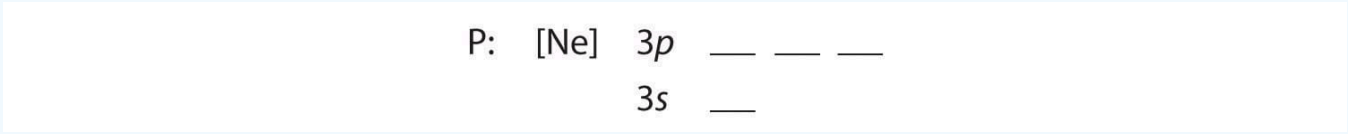
Strategy:

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.
B. Referring to Figure 2.7.1, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.
C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

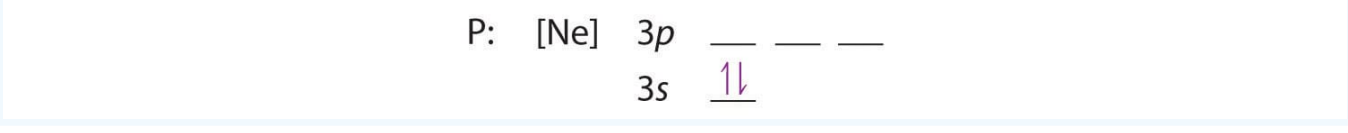
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

B The additional five electrons are placed in the next available orbitals, which are the 3*s* and 3*p* orbitals:



Because the 3s orbital is lower in energy than the 3*p* orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:

P: [Ne] 3*p* ↑ ↑ ↑
3*s* ↑↓

The electron configuration is [Ne]$3s^2 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives 5 valence electrons ($3s^2 3p^3$).

Exercise 2.7.1

What is the electron configuration of chlorine, Z = 17? How many valence electrons does it have?

Answer available at the end of this section.

Energy of Orbitals

The general order in which orbitals are filled is depicted in Figure 2.7.2. Subshells corresponding to each value of *n* are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4s orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton (*Z* = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4s, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5s, 4*d*, and 5*p* orbitals are filled sequentially.

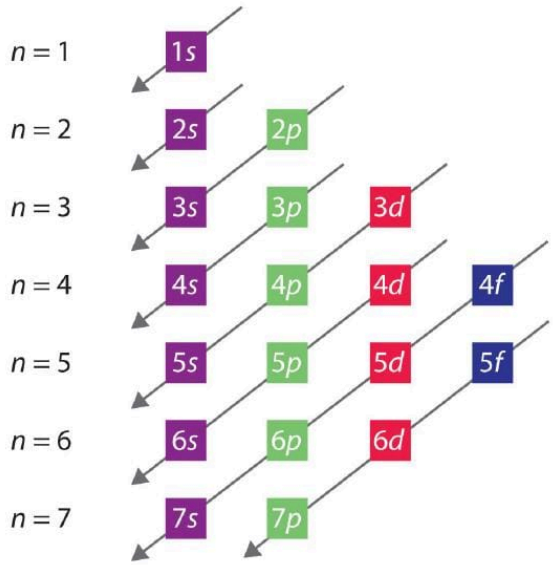


Figure 2.7.2: Predicting the Order in Which Orbitals Are Filled in Multi-electron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

Example 2.7.2: Electron Configuration of Zinc

Write the electron configuration of zinc (Z = 30), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 2.7.1 and the periodic table as a guide, fill the orbitals until all 30 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 2.7.2 and using the periodic table as a guide, we obtain

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10}$	row 4	12 electrons

The result is the electron configuration of zinc:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} = [Ar]4s^2 3d^{10}$$

(You should always check to be sure that the total number of electrons equals the atomic number.)

The electron configurations of the elements are presented in Figure 2.7.2, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted. Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is $[Ar]4s^1 3d^5$ rather than the predicted $[Ar]4s^2 3d^4$. Similarly, the observed electron configuration of copper is $[Ar]4s^1 3d^{10}$ instead of $[Ar]s^2 3d^9$. These anomalies are related to the energetic stability of filled, or partially filled, d-orbitals, however in CHM 135H we will not deal with any anomalous electron configurations.

Since the arrangement of the periodic table is based on the electron configurations, Figure 2.7.3 shows how the table is organized into an s-block (Groups 1 and 2) where the s-orbital is being filled, the p-block (Groups 13-18) where the p-orbitals are being filled, and the d-block (Groups 3-12) where the d-orbitals are being filled. This demonstrates how the periodic table can be used to predict the electron configuration of an atom using its position on in the table.

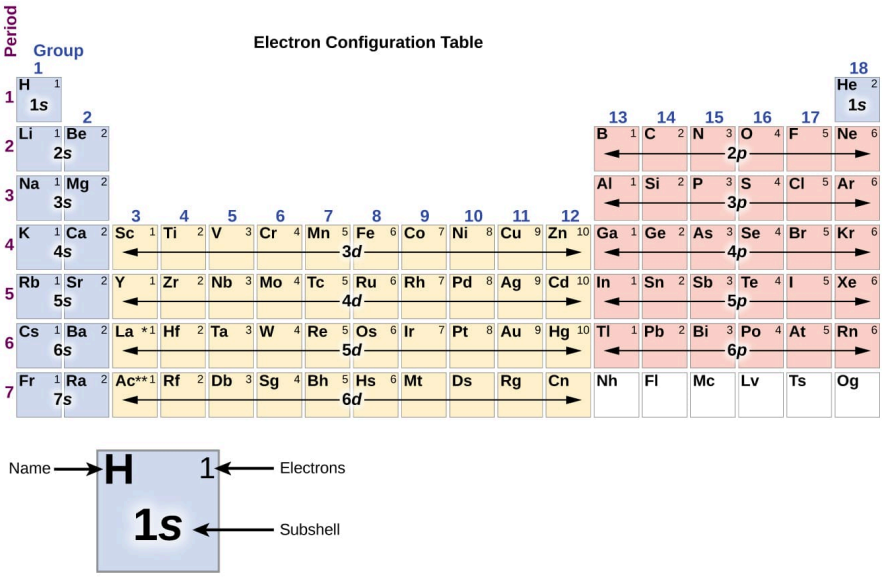


Figure 2.7.3: This partial periodic table shows electron configurations for the valence subshells of atoms. By “building up” from hydrogen, this table can be used to determine the electron configuration for atoms of most elements in the periodic table. (Electron configurations of the lanthanides and actinides are not accurately predicted by this simple approach.

For example, to find the electron configuration of As, you would start at the hydrogen and move from left to right across the rows: $1s^2$, and then to the next row $2s^2$, $2p^6$, and then to the next row, $3s^2$, $3p^6$, and then to the next row, $4s^2$, $3d^{10}$, $4p^3$ until As is reached, giving the electron configuration:

As: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$ or $[Ar]4s^2 3d^{10} 4p^3$

The periodic table is a convenient tool for determining electron configuration.

Summary

Using quantum mechanics, we determine electron configurations based on:

- The Pauli exclusion principle (each orbital holds two electrons with opposite spins).
- The Aufbau principle (electrons fill lowest-energy orbitals first).
- Hund’s rule (electrons spread out in a subshell before pairing).

For chemical reactions, the valence electrons (electrons in the outermost principal shell) are the most important. Since elements in the same group have the same valence electron configurations, they exhibit similar chemical properties.

Glossary

Aufbau principle
: Dictates the 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.

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

Hund's rule
: States that 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
: A pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow.

valence electron

An electron in the outermost or valence shell (highest value of n) of a ground-state atom; determines how an element reacts.

Answers

Exercise 2.7.1

[Ne]$3s^2 3p^5$; 7 valence electrons $3s^2 3p^5$

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2.8: Trends in Atomic Size

Learning Objectives

- Describe and explain the observed trends in atomic radii moving across a row or down a group of the periodic table.
- Describe how ion formation affect the size.
- Arrange by size a series of isoelectronic ions

Elements in the same group (vertical column) of the periodic table exhibit similar chemical behaviour because they 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. In this section we will focus on periodic trends in atomic size or radius.

Atomic Radii

Because electrons are described as probability distributions, defining the exact size of an atom is difficult. Instead, we use covalent radius (Figure 2.8.1), which is half the distance between the nuclei of two identical atoms bonded together.

The trend in atomic size follows two key patterns:

- Atomic size increases down a group (or column) because electrons occupy orbitals farther from the nucleus as n increases.
- Atomic size decreases across a period (or row) because effective nuclear charge (Z_{eff}) increases, pulling electrons closer to the nucleus.

Each step down a group corresponds to an increase in n, which means electrons are in orbitals that extend farther from the nucleus. As a result, atomic size increases down a group, as seen in the halogen group (Table 2.8.1). The trends for the entire periodic table can be seen in part b of Figure 2.8.1.

Table 2.8.1: 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

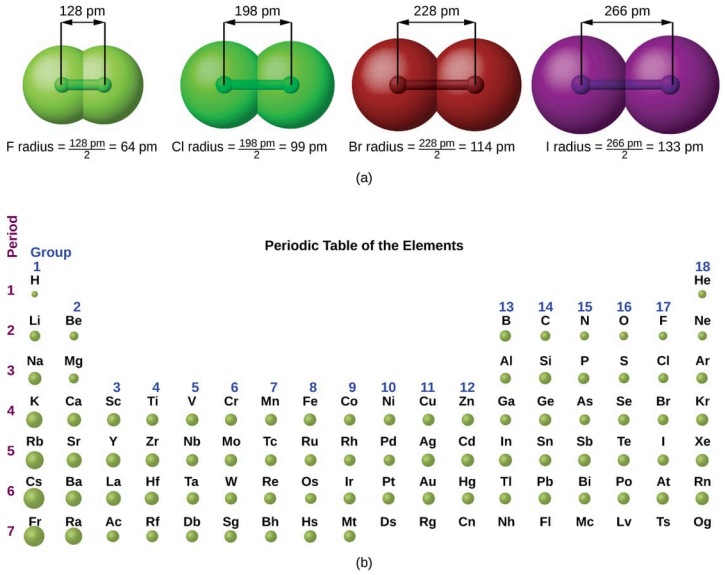


Figure 2.8.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

Although more electrons are being added as we move from left to right, atomic size (Figure 2.8.1) decreases because of the increasing effective nuclear charge (Z_{eff}).

- Z_{eff} is the net positive charge experienced by an electron, considering both attraction to the nucleus and shielding by inner electrons.
- Core (inner) electrons shield valence electrons effectively, but electrons in the same shell do not shield each other as well.
- As a result, Z_{eff} increases across a period, drawing electrons closer to the nucleus and making the atomic radius smaller

Thus, atomic radius decreases across a period despite the increasing number of electrons.

Example 2.8.1: Sorting Atomic Radii

Using only the periodic table, place the following atoms in order of increasing covalent radius:

Ge, Fl, Br, Kr.

Solution

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

Exercise 2.8.1

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

Answer available at the end of this section.

Ionic Radii

Ionic radius describes the size of an ion. A cation, a positively-charged ion, 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 2.8.2). 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 Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. When the outer $3s^2$ and

$3p^1$ electrons are removed, the remaining core electrons in the n = 2 shell are closer to the nucleus, making Al^{3+} significantly smaller than neutral Al.



Figure 2.8.2: 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.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 2.8.2). For example, a sulfur atom ([Ne]$3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ([Ne]$3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions with the same electron configuration are called isoelectronic. In an isoelectronic series, size depends on nuclear charge (*Z*) — higher *Z* results in a smaller radius because the electrons are pulled in more tightly.

For example, the following species are isoelectronic with Ne ([Ne] = $1s^2 2s^2 2p^6$):

N^{3-} (7 protons) > O^{2-} (8 protons) > F^- (9 protons) > Ne (10 protons) > Na^+ (11 protons) > Mg^{2+} (12 protons) > Al^{3+} (13 protons)

Since all have the same number of electrons, the species with the most protons (Al^{3+}) is smallest, while the species with the fewest protons (N^{3-}) is largest.

Summary

Electron configurations allow us to understand many periodic trends. Atomic radius increases as we move down a group because the *n* level (orbital size) increases. Atomic 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. Within an isoelectronic series of ions, the size will depend on the number of protons with more protons resulting in a smaller size.

Glossary

covalent radius
: One-half the distance between the nuclei of two identical bonded atoms.

ionic radius
: Measure of an ion's size, where cations are larger than the parent atom and anions are smaller.

isoelectronic
: Describes a group of ions or atoms that have identical electron configurations.

Answers

Exercise 2.8.1

Ne or He

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2.E: Quantum Theory and Electronic Structure (Exercises)

The Nature of Light

Exercise $2.E.1$*

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.03 \times 10^{8}\ s^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

Answer available at the end of this section.

Exercise $2.E.2$*

FM-95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^{7}\ s^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?

Answer available at the end of this section.

Exercise $2.E.3$*

A bright violet line occurs at 436 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

Answer available at the end of this section.

Exercise $2.E.4$*

Light with a wavelength of 615 nm looks orange. What is the energy, in joules, per photon of this orange light?

Answer available at the end of this section.

Exercise $2.E.5$**

Heated lithium atoms emit photons of light with an energy of 2.96×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the energy of 1 mole of these photons?

Answer available at the end of this section.

Exercise $2.E.6$**

A photon of light produced by a surgical laser has an energy of 3.03×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons?

Answer available at the end of this section.

Exercise 2.E.7*

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines?

Answer available at the end of this section.

Exercise 2.E.8*

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.09×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

Answer available at the end of this section.

Exercise 2.E.9***

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

Answer available at the end of this section.

Exercise 2.E.10***

Answer the following questions about a Blu-ray laser:

a) The laser on a Blu-ray player has a wavelength of 405 nm. Using Figure 2.1.4, determine the region of the electromagnetic spectrum. What is its frequency?

b) A Blu-ray laser has a power of 5 milliwatts (1 Watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?

Answer available at the end of this section.

Atomic Spectra

Exercise 2.E.11**

What does it mean to say that the energy of the electrons in an atom is quantized?

Answer available at the end of this section.

Exercise 2.E.12*

Which of the following transitions correspond to emission and which to absorption?

a) n = 2 to n = 3

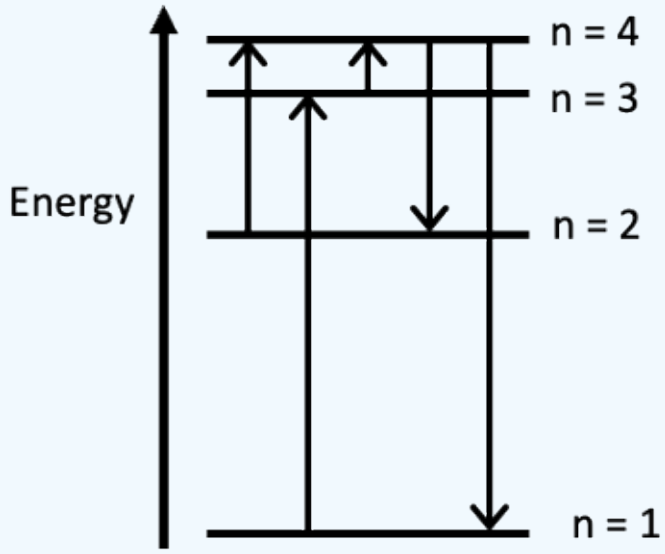
b) n = 3 to n = 1

c) n = 5 to n = 4

Answer available at the end of this section.

Exercise $2.E.13$**

Several electronic transitions in a hydrogen atom are shown by the arrows on the energy diagram below. Which arrow represents the absorption of light of the shortest wavelength?



Answer available at the end of this section.

Exercise $2.E.14$**

Consider a large number of hydrogen atoms with electrons randomly distributed in the n = 1, 2, 3, and 4 levels.

a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy levels?

b) Calculate the highest energy of light produced by the transitions described in part (a). What is the frequency and wavelength of this light?

c) Calculate the lowest energy of light produced by the transitions described in part (a). What is the frequencies and wavelength of this light?

Answer available at the end of this section.

Exercise $2.E.15$*

Determine the energy of an electron with $n = 6$ in a hydrogen atom.

Answer available at the end of this section.

Exercise $2.E.16$*

Determine the energy of an electron with $n = 8$ in a hydrogen atom.

Answer available at the end of this section.

Exercise $2.E.17$**

Determine the energy, of the photon produced when an electron in a hydrogen atom moves from the $n = 5$ level to $n = 2$ level.

Answer available at the end of this section.

Exercise $2.E.18$**

An electron in the n = 5 level of a hydrogen atom emits a photon with a wavelength of 1281 nm. What is the energy level of the electron after the transition?

Answer available at the end of this section.

Exercise $2.E.19$***

An electron in the ground state of a hydrogen atom absorbs a photon with a wavelength of 93.79 nm to transition to a different energy level. The atom then emits two photons. The first photon has a wavelength of 2626 nm which brings the electron to another energy level. An additional photon is emitted to return the electron to the ground state.

a) What is the energy level of the electron after the initial absorption?

b) What is the energy level of the electron after the emission of the first photon with a wavelength of 2626 nm?

c) What is the wavelength of the second photon emitted to return the electron to the ground state?

Answer available at the end of this section.

The Quantum Mechanical Model of the Atom

Exercise $2.E.20$*

What are the allowed values for the four quantum numbers: n, l, m_l, and m_s?

Answer available at the end of this section.

Exercise $2.E.21$*

Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

Answer available at the end of this section.

Exercise $2.E.22$*

Define the shell and subshell of an atom.

Answer available at the end of this section.

Exercise $2.E.23$*

Identify the subshell in which electrons with the following quantum numbers are found:

(a) n = 2, l = 1

(b) n = 4, l = 2

(c) n = 6, l = 0

Answer available at the end of this section.

Exercise $2.E.24$*

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

Answer available at the end of this section.

Exercise $2.E.25$**

(a) What is the maximum number of electrons contained in an s orbital? A p orbital? A d orbital?

(b) How many s, p, and d orbitals are in the n = 2 shell?

(c) Write a set of four quantum numbers for an electron in a 4s orbital.

(d) Write a set of four quantum numbers for an electron in a 2p orbital.

(e) Write a set of four quantum numbers for an electron in a 3d orbital.

(f) What is the smallest possible n value for a d orbital?

Answer available at the end of this section.

Exercise $2.E.26$*

For each of the following, give the sublevel designation and the number of orbitals:

(a) n = 4, l = 2

(b) n = 5, l = 1

(c) n = 3, l = 0

Answer available at the end of this section.

Many Electron Atoms

Exercise $2.E.27$*

What does the Pauli exclusion principle tell us about how electrons fill orbitals?

Answer available at the end of this section.

Exercise $2.E.28$***

Compare the 2s and 2p orbitals in a polyatomic atom. Which orbital is more penetrating? Which orbital experiences less shielding? Which orbital is lower in energy?

Answer available at the end of this section.

Electronic Configurations

Exercise $2.E.29$*

Write the full electron configuration of each of the following atoms:

(a) C

(b) P

(c) Sb

Answer available at the end of this section.

Exercise $2.E.30$*

Write the full electron configuration of each of the following atoms:

(a) N

(b) Si

(c) Te

Answer available at the end of this section.

Exercise $2.E.31$*

Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

(a) N

(b) Si

Answer available at the end of this section.

Exercise $2.E.32$*

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^4$?

Answer available at the end of this section.

Exercise $2.E.33$*

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$?

Answer available at the end of this section.

Exercise $2.E.34$*

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

Answer available at the end of this section.

Exercise $2.E.35$**

Which of the following has two unpaired electrons: Mg, Si, S?

Answer available at the end of this section.

Exercise $2.E.36$**

Write a set of quantum numbers for each of the electrons with n = 4 in a Se atom.

Answer available at the end of this section.

Exercise $2.E.37$**

Write the electron configurations for the following ions:

(a) N^{3-}

(b) Ca^{2+}

(c) S^{-}

(d) Cl^{-}

Answer available at the end of this section.

Trends in Atomic Size

Exercise $2.E.38$*

Using a periodic table only, predict which of the following atoms is the smallest:

Mg, Sr, Si, Cl, I

Answer available at the end of this section.

Exercise $2.E.39$*

Using a periodic table only, predict which of the following atoms has the largest atomic radius:

Li, Rb, N, F, I

Answer available at the end of this section.

Exercise $2.E.40$*

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs

Answer available at the end of this section.

Exercise $2.E.41$*

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl

Answer available at the end of this section.

Exercise $2.E.42$**

The ionic radii of the ions S^{2-}, Cl^{-}, and K^{+} are 184, 181, and 138 pm, respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

Answer available at the end of this section.

Answer available at the end of this section.

Additional Problems

Exercise $2.E.43$**

Write a full set of quantum numbers for

(a) the electron lost when K becomes K^{+}

(b) the electron gained when Cl becomes Cl-

(c) the highest energy electron in a ground state Al atom

Answer available at the end of this section.

Exercise $2.E.44$**

An electron in the n = 2 level of a hydrogen atom absorbs a photon with a wavelength of 486.3 nm. What is the energy level of the electron after the transition?

Answer available at the end of this section.

Exercise $2.E.45$***

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C, which requires 11 kJ of energy?

Answer available at the end of this section.

Exercise $2.E.46$***

Determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. How much energy would be required to ionize a mole of hydrogen atoms?

Answer available at the end of this section.

Exercise $2.E.47$**

Which of the following sets of quantum numbers are allowed?

(a) n = 1, l = 1, m_l = 1, m_s = -½

(b) n = 2, l = 0, m_l = 1, m_s = ½

(c) n = 2, l = 1, m_l = 2, m_s = -½

(d) n = 3, l = 2, m_l = 1, m_s = ½

Answer available at the end of this section.

Exercise $2.E.48$**

Which of the following quantum numbers can describe an electron in a ground-state magnesium (Mg) atom?

a) n = 2, l = 2, m_l = 1, m_s = ½

b) n = 3, l = 2, m_l = -1, m_s = -½

c) n = 3, l = 1, m_l = 2, m_s = ½

d) n = 3, l = 1, m_l = -1, m_s = -½

e) n = 2, l =1, m_l = 0, m_s = ½

Answer available at the end of this section.

Answers

Exercise $2.E.1$*

$$\lambda = \frac{c}{\nu}$$
$$\lambda = \frac{3.00 \times 10^8 \ \frac{m}{s}}{1.03 \times 10^8 \ \frac{1}{s}} = 2.91 \ m$$

Exercise $2.E.2$*

$$\lambda = \frac{c}{\nu}$$
$$\lambda = \frac{3.00 \times 10^8 \ \frac{m}{s}}{9.51 \times 10^7 \ \frac{1}{s}} = 3.15 \ m$$

Exercise $2.E.3$*

$$E = \frac{hc}{\lambda}$$
$$E = \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}} \left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)}{436 \text{ nm}} \left(\frac{10^9 \text{ nm}}{\text{m}}\right)$$
$$= 4.56 \times 10^{-19} J$$

Exercise $2.E.4$*

$$E = \frac{hc}{\lambda}$$
$$E = \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}} \left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)}{615 \text{ nm}} \left(\frac{10^9 \text{ nm}}{\text{m}}\right)$$
$$= 3.23 \times 10^{-19} J$$

Exercise $2.E.5$**

$$E = h\nu \ \ \nu = \frac{E}{h} = \frac{2.96 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 4.47 \times 10^{14} \text{ s}^{-1}$$
$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{4.47 \times 10^{14} \text{ s}^{-1}} = 6.72 \times 10^{-7} \text{ m}$$

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ photons}$$
$$E = 2.96 \times 10^{-19} \text{ J} \left(\frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}}\right)$$
$$= 1.78 \times 10^5 \text{ J}$$

Exercise $2.E.6$**

$$E = h\nu \ \ \nu = \frac{E}{h} = \frac{3.03 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 4.57 \times 10^{14} \text{ s}^{-1}$$
$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{4.57 \times 10^{14} \text{ s}^{-1}} = 6.56 \times 10^{-7} \text{ m}$$

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ photons}$$
$$E = 3.03 \times 10^{-19} \text{ J} \left(\frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}}\right)$$
$$= 1.82 \times 10^5 \text{ J}$$

Exercise $2.E.7$*

a)

$$\lambda = \frac{c}{v} = \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}}}{3.45 \times 10^{14} \text{ s}^{-1}} = 8.70 \times 10^{-7} \text{ m}$$
$$E = h\nu = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \left(3.45 \times 10^{14} \text{ s}^{-1}\right)$$
$$= 2.29 \times 10^{-19} \text{ J}$$

b)

$$\lambda = \frac{c}{v} = \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}}}{6.53 \times 10^{14} \text{ s}^{-1}} = 4.59 \times 10^{-7} \text{ m}$$
$$E = h\nu = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \left(6.53 \times 10^{14} \text{ s}^{-1}\right) = 4.33 \times 10^{-19} \text{ J}$$

Exercise $2.E.8$*

$$E = \frac{hc}{\lambda}$$
$$E = \frac{3.00 \times 10^{8}\,\text{m/s} \times 6.626 \times 10^{-34}\,\text{J} \cdot \text{s}}{2.09 \times 10^{-11}\,\text{m}}$$
$$E = 9.51 \times 10^{-15}\,\text{J}$$

$$\nu = \frac{c}{\lambda}$$
$$\nu = \frac{3.00 \times 10^{8}\,\text{m/s}}{2.09 \times 10^{-11}\,\text{m}}$$
$$\nu = 1.44 \times 10^{19}\,\text{Hz}$$

Exercise $2.E.9$***

We can calculate the energy of each photon because we know the wavelength of the photon:

$$E = \frac{hc}{\lambda}$$
$$E = \frac{3.00 \times 10^{8}\,\text{m/s} \times 6.626 \times 10^{-34}\,\text{J} \cdot \text{s}}{850\,\text{nm}} \times \left(\frac{10^{9}\,\text{nm}}{1\,\text{m}}\right)$$
$$E = 2.34 \times 10^{-19}\,\text{J}$$

Then we need to find out how many of these photons it will take to trip the visual signal to the brain:

$$\frac{3.15 \times 10^{-14}\ \cancel{J}}{2.34 \times 10^{-19}\ \frac{\cancel{J}}{\text{photon}}}$$
$$= 1.35 \times 10^{5}\,\text{photons}$$

Exercise $2.E.10$***

a) Looking at Figure 2.1.4, we can see that 405 nm is in the visible region (violet) of the electromagnetic spectrum. **Note: you do not need to memorize the wavelengths of the electromagnetic spectrum.**

$$\nu = \frac{c}{\lambda}$$
$$\nu = \frac{3.00 \times 10^{8}\,\text{m/s}}{405\,\text{nm}} \times \left(\frac{10^{9}\,\text{nm}}{1\,\text{m}}\right)$$
$$\nu = 7.41 \times 10^{14}\,\text{Hz}$$

b) We can find the total energy that is produced in an hour by the laser:

$$5\ \text{mW}\left(\frac{\text{W}}{1000\ \text{mW}}\right)\left(\frac{\text{J/s}}{\text{W}}\right)(1\text{hr})\left(\frac{60\ \text{min}}{\text{hr}}\right)\left(\frac{60\ \text{s}}{\text{min}}\right) = 18\ \text{J}$$

We can also find the energy of each photon:

$$E = \frac{hc}{\lambda}$$
$$E = \frac{3.00 \times 10^{8}\,\text{m/s} \times 6.626 \times 10^{-34}\,\text{J} \cdot \text{s}}{405\ \text{nm}}\left(\frac{10^{9}\ \text{nm}}{\text{m}}\right)$$
$$E = 4.91 \times 10^{-19}\,\text{J}$$

The number of photons is the total energy divided by the energy per photon:

$$\frac{18\ \cancel{J}}{4.91 \times 10^{-19}\ \frac{\cancel{J}}{photon}} = 4 \times 10^{19}\,photons$$

Exercise $2.E.11$**

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

Exercise $2.E.12$*

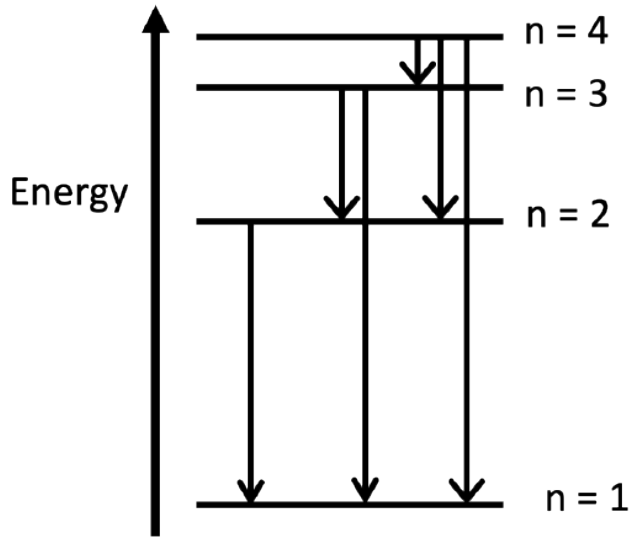
Emission of a photon occurs when the electron moves to a lower energy level (i.e. on average closer to the nucleus). Both b) and c) are emissions. Absorption of a photon occurs as an electron moves to a higher energy level as in a).

Exercise $2.E.13$**

Absorption of a photon occurs as an electron moves to a higher energy level, so n = 1 to n = 3, n = 2 to n = 4 and n = 3 to n = 4 all represent absorption. The energy of the photon absorbed is equal to the difference in energy between the levels. The shorter wavelength of light corresponds to the biggest difference in energy because E is inversely proportional to wavelength, $E = \frac{hc}{\lambda}$. Therefore, the arrow representing absorption of the shortest wavelength of light is n = 1 to n = 3.

Exercise $2.E.14$**

a) From n = 4, the electron can fall to either n = 3, n = 2 or n = 1. From n = 3, the electron can fall to either n = 2 or n = 1. From n = 2 the electron can fall to n = 1. This corresponds to 6 different changes in energy and therefore 6 different wavelengths of light emitted.



b) The highest energy of light corresponds to the biggest change in energy. This is from n = 4 to n = 1. We can use Equation 2.2.3 to calculate this energy difference:

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = -2.04 \times 10^{-18}$$

This value of ΔE is negative indicating that energy is lost from the atom. The energy of the photon emitted is 2.04 x 10^{-18} J.
To find the frequency and wavelength of the light:

$$E = h\nu \;\; \nu = \frac{E}{h} = \frac{2.04 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 3.08 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8} \text{ m/s}}{3.08 \times 10^{15} \text{ s}^{-1}} = 9.74 \times 10^{-8} \text{ m}$$

c) The lowest energy of light corresponds to the smallest change in energy. Since the energy levels get closer together with increased values of n, this corresponds to n = 4 to n = 3. We can use Equation 2.2.3 to calculate this energy difference:

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18} \left(\frac{1}{3^2} - \frac{1}{4^2} \right) = -1.06 \times 10^{-19}$$

This value of ΔE is negative indicating that energy is lost from the atom. The energy of the photon emitted is 1.06 x 10^{-19} J.
To find the frequency and wavelength of the light:

$$E = h\nu \;\; \nu = \frac{E}{h} = \frac{1.06 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 1.60 \times 10^{14} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8} \text{ m/s}}{1.60 \times 10^{14} \text{ s}^{-1}} = 1.88 \times 10^{-6} \text{ m}$$

Exercise $2.E.15$*

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{n^2} \right)$$

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{6^2} \right) = -6.06 \times 10^{-20} J$$

Exercise $2.E.16$*

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{n^2} \right)$$

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{8^2} \right) = -3.41 \times 10^{-20} J$$

Exercise $2.E.17$**

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18} \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = -4.58 \times 10^{-19}$$

This value of ΔE is negative indicating that energy is lost from the atom. The energy of the photon emitted is 4.58 x 10^{-19} J.

Exercise $2.E.18$**

Given the wavelength of the photon, we can calculate the energy of the photon:

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{\left(6.626 \times 10^{-34}\text{J} \cdot \text{s}\right)\left(\frac{3\times10^{8}\text{ m}}{\text{s}}\right)}{1281\text{ nm}}\left(\frac{10^{9}\text{ nm}}{\text{m}}\right) = 1.55 \times 10^{-19}\text{ J}$$

The electron is initially in the n = 5 state so we can calculate the initial energy:

$$E_5 = -2.18 \times 10^{-18} J\left(\frac{1}{5^2}\right) = -8.72 \times 10^{-20} J$$

Once the photon is emitted, the electron moves to lower energy and we can calculate the energy at the new level. Note that the gap between the energy levels is equal to the energy of the photon and since it is emitted energy is lost from the atom, i.e. $\Delta E = -1.55 \times 10^{-19}$ J.
$\Delta E = E_n - E_5$

$$E_n = -8.72 \times 10^{-20} J - 1.55 \times 10^{-19} J = -2.42 \times 10^{-19} J$$

We can then determine the value of n:

$$E_n = -2.18 \times 10^{-18} J\left(\frac{1}{n^2}\right) = -2.42 \times 10^{-19} J$$

$$n^2 = 9 \quad n = 3$$

Exercise $2.E.19$***

a) Given the wavelength of the photon, we can calculate the energy of the photon:

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{\left(6.626 \times 10^{-34}\text{ J} \cdot \text{s}\right)\left(\frac{3\times10^{8}\text{ m}}{\text{s}}\right)}{93.79\text{ nm}}\left(\frac{10^{9}\text{ nm}}{\text{m}}\right) = 2.119 \times 10^{-18}\text{ J}$$

The electron is initially in the n = 1 state so we can calculate the initial energy:

$$E_1 = -2.18 \times 10^{-18} J\left(\frac{1}{1^2}\right) = -2.18 \times 10^{-18} J$$

Once the photon is absorbed, the electron moves to higher energy and we can calculate the energy at the new level. Note that the gap between the energy levels is equal to the energy of the photon and since it is absorbed, energy is gained to the atom, i.e. $\Delta E = 2.119 \times 10^{-18}$ J.
$\Delta E = E_n - E_1$

$$E_n = 2.119 \times 10^{-18} J - 2.18 \times 10^{-18} J = -6.058 \times 10^{-20} J$$

We can then determine the value of n:

$$E_n = -2.18 \times 10^{-18} J\left(\frac{1}{n^2}\right) = -6.058 \times 10^{-20} J$$

$$n^2 = 36 \quad n = 6$$

b) Given the wavelength of the photon, we can calculate the energy of the photon:

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{\left(6.626 \times 10^{-34}\text{ J} \cdot \text{s}\right)\left(\frac{3\times10^{8}\text{ m}}{\text{s}}\right)}{2626\text{ nm}}\left(\frac{10^{9}\text{ nm}}{\text{m}}\right) = 7.57 \times 10^{-20}\text{ J}$$

The electron is initially in the n = 6 state so we can calculate the initial energy:

$$E_6 = -2.18 \times 10^{-18} J\left(\frac{1}{6^2}\right) = -6.06 \times 10^{-20} J$$

Once the photon is emitted, the electron moves to lower energy and we can calculate the energy at the new level. Note that the gap between the energy levels is equal to the energy of the photon and since it is emitted energy is lost from the atom, i.e. $\Delta E = -7.57 \times 10^{-20}$ J.
$\Delta E = E_n - E_6$

$$E_n = -7.57 \times 10^{-20} J - 6.06 \times 10^{-20} J = -1.36 \times 10^{-19} J$$

We can then determine the value of n:

$$E_n = -2.18 \times 10^{-18} J\left(\frac{1}{n^2}\right) = -1.36 \times 10^{-19} J$$

$$n^2 = 16 \quad n = 4$$

c) The final transition is from n = 4 (from part b) to n = 1, the ground state.

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18}\left(\frac{1}{1^1} - \frac{1}{4^2}\right) = -2.04 \times 10^{-18}$$

This value of ΔE is negative indicating that energy is lost from the atom, i.e. the photon is emitted. The energy of the photon emitted is 2.04×10^{-18} J.
To find the wavelength:

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{\left(6.626 \times 10^{-34}\text{ J} \cdot \text{s}\right)\left(3.00 \times 10^{8}\text{ m/s}\right)}{2.04 \times 10^{-18}\text{ J}} = 9.73 \times 10^{-8}\text{ m}$$

Video solutions:
Part a)
Part b)
Part c)

Exercise $2.E.20$*

n is the principal quantum number and can be any positive integer.

l is the angular momentum quantum number and can have values from 0 to n-1.

m_l is the magnetic quantum number and can have values from -l to +l.

m_s is the spin quantum number and can have values of +1/2 or -1/2.

Exercise $2.E.21$*

n determines the energy and the relative size of the orbital. l determines the shape of the orbital. m_l determines the orientation of the orbitals. m_s determines the spin of an electron.

Exercise $2.E.22$*

Orbitals with the same value of n are in the same shell. Orbitals with the same value of n and l are in the same subshell.

Exercise $2.E.23$*

(a) 2p; (b) 4d; (c) 6s

Exercise $2.E.24$*

2p has three degenerate orbitals. 4d has five degenerate orbitals. 6s has a single orbital.

Exercise $2.E.25$**

(a) Each orbital can contain 2 electrons.

(b) There is one s orbital and three p orbitals in the n = 2 shell.

(c) From the 4s designation, we know that the n value is 4 and the l value is 0. Since m_l values depend on l (-l to l), the only possible m_l is 0.

n = 4, l = 0, m_l = 0, m_s = 1/2 or -1/2

(d) From the 2p designation, we know that the n value is 2 and the l value is 1. Since m_l values depend on l (-l to l), the possible m_l values are -1, 0, or 1.

Possible sets of quantum numbers:

n = 2, l = 1, m_l = -1, m_s = 1/2 or -1/2

n = 2, l = 1, m_l = 0, m_s = 1/2 or -1/2

n = 2, l = 1, m_l = 1, m_s = 1/2 or -1/2

(e) From the 3d designation, we know that the n value is 3 and the l value is 2. Since m_l values depend on l (-l to l), the possible m_l values are -2, -1, 0, 1, or 2.

Possible sets of quantum numbers:

n = 3, l = 2, m_l = -2, m_s = 1/2 or -1/2

n = 3, l = 2, m_l = -1, m_s = 1/2 or -1/2

n = 3, l = 2, m_l = 0, m_s = 1/2 or -1/2

n = 3, l = 2, m_l = 1, m_s = 1/2 or -1/2

n = 3, l = 2, m_l = 2, m_s = 1/2 or -1/2

(f) A d orbital has l = 2. Since l has allowed values of 0 to n-1, the smallest possible n value is 3.

Exercise $2.E.26$*

(a) 4d, five orbitals (possible m_l values: -2, -1, 0, 1, 2)

(b) 5p, three orbitals (possible m_l values: -1, 0, 1)

(c) 3s, one orbital (m_l value: 0)

Exercise $2.E.27$*

Each orbital can only contain two electrons with opposing spins, +1/2 and -1/2.

Exercise $2.E.28$***

The 2s orbital is more penetrating because it has a significant probability of finding the electron very close to the nucleus. Because of this penetration the 2s orbital experiences less shielding and is lower in energy than the 2p orbital.

Exercise $2.E.29$*

(a) $1s^2 2s^2 2p^2$

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

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^3$

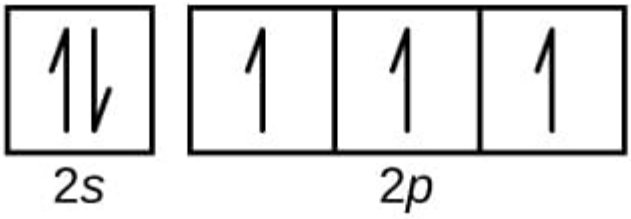
Exercise $2.E.30$*

(a) $1s^2 2s^2 2p^3$

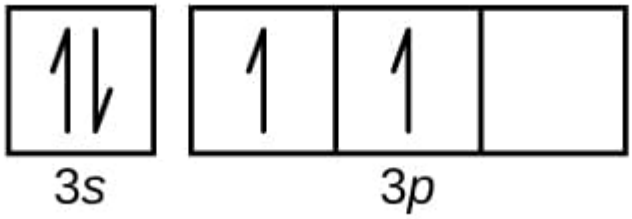
(b) $1s^2 2s^2 2p^6 3s^2 3p^2$

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$

Exercise $2.E.31$*



a)



b)

Exercise $2.E.32$*

S

Exercise $2.E.33$*

Ga

Exercise $2.E.34$*

B: $1s^2 2s^2 2p^1$

Exercise $2.E.35$**

Mg: $1s^2 2s^2 2p^6 3s^2$. No unpaired electrons.

Si: $1s^2 2s^2 2p^6 3s^2 3p^2$. The electrons in the 3p subshell would be in two different p orbitals, so 2 unpaired electrons.

S: $1s^2 2s^2 2p^6 3s^2 3p^4$. One 3p orbital would contain 2 paired electrons. The other two 3p orbitals would have one unpaired electron, so 2 unpaired electrons.

Si and S

Exercise $2.E.36$**

The electron configuration of Se is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$, so the orbitals with n = 4 are the 4s and 4p orbitals.

n	*l*	m_l	*s*
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	–1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	–1	$-\frac{1}{2}$

The three 4p orbitals are degenerate (have the same energy), so it doesn't matter which m_l value you choose for the 4p orbital that is filled.

Exercise $2.E.37$**

(a) N: $1s^2 2s^2 2p^3$; N^{3-} has 3 additional electrons, so $1s^2 2s^2 2p^6$

(b) Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$; Ca^{2+} has lost two electrons, so $1s^2 2s^2 2p^6 3s^2 3p^6$

(c) S: $1s^2 2s^2 2p^6 3s^2 3p^4$; S^- has gained one electron, so $1s^2 2s^2 2p^6 3s^2 3p^5$

(d) Cl:$1s^2 2s^2 2p^6 3s^2 3p^5$; Cl^- has gained one electron, so $1s^2 2s^2 2p^6 3s^2 3p^6$

Exercise $2.E.38$*

Cl

Exercise $2.E.39$*

Rb

Exercise $2.E.40$*

Mg < Ca < Rb < Cs

Exercise $2.E.41$*

Cl < Si < Ca < Sr

Exercise $2.E.42$**

Exercise $2.E.42$**

While the ions have the same number of electrons, they do not have the same number of protons. K^+ has the largest number of protons and therefore electrons in this cation will experience the highest effective nuclear charge, making it the smallest of the three ions.

Exercise $2.E.43$**

(a) K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ To form K^+, the electron in the highest energy orbital, 4s, is lost.

n = 4, l = 0, m_l = 0, m_s = +1/2 or -1/2

(b) Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ To form Cl^-, the electron is gained to fill the 3p orbital.

Possible quantum numbers:

n = 3, l = 1, m_l = 1, m_s = +1/2 or -1/2

n = 3, l = 1, m_l = 0, m_s = +1/2 or -1/2

n = 3, l = 1, m_l = -1, m_s = +1/2 or -1/2

(c) Al: $1s^2 2s^2 2p^6 3s^2 3p^1$ The highest energy electron is in a 3p orbital.

Possible quantum numbers:

n = 3, l = 1, m_l = 1, m_s = +1/2 or -1/2

n = 3, l = 1, m_l = 0, m_s = +1/2 or -1/2

n = 3, l = 1, m_l = -1, m_s = +1/2 or -1/2

Exercise $2.E.44$**

Given the wavelength of the photon, we can calculate the energy of the photon:

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{J} \cdot \text{s})\left(\frac{3\times10^8\ \text{m}}{\text{s}}\right)}{486.3\ \text{nm}}\left(\frac{10^9\ \text{nm}}{\text{m}}\right) = 4.088 \times 10^{-19}\ \text{J}$$

The electron is initially in the n = 2 state so we can calculate the initial energy:

$$E_2 = -2.18 \times 10^{-18} J \left(\frac{1}{2^2}\right) = -5.45 \times 10^{-19} J$$

Once the photon is absorbed, the electron moves to higher energy and we can calculate the energy at the new level. Note that the gap between the energy levels is equal to the energy of the photon and since it is absorbed energy is gained to the atom, i.e. ΔE = 4.088 x 10^{-19} J.

$\Delta E = E_n - E_2$

$$E_n = 4.088 \times 10^{-19} J - 5.45 \times 10^{-19} J = -1.36 \times 10^{-19} J$$

We can then determine the value of n:

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{n^2}\right) = -1.36 \times 10^{-19} J$$

$$n^2 = 16 \quad n = 4$$

Exercise $2.E.45$***

We can calculate the energy of each photon because we know the wavelength of the photon:

$$E = \frac{hc}{\lambda}$$

$$E = \frac{3.00 \times 10^8\ \text{m/s} \times 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}}{1.5 \times 10^{-6}\ \text{m}}$$

$$E = 1.3 \times 10^{-19}\ \text{J}$$

This is the energy of one photon, so now we have to see how many photons we need to give 11 kJ of energy:

$$\frac{11,000\ J}{1.3 \times 10^{-19}\ \frac{J}{photon}} = 8.3 \times 10^{22} photons$$

Exercise $2.E.46$***

Ionize means to remove the electron from the atom completely which can be shown as n = ∞.

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18}\left(\frac{1}{\infty^2} - \frac{1}{1^2}\right) = 2.18 \times 10^{-18}\ \text{J}$$

To ionize a mol of hydrogen atoms means to ionize 6.022 x 10^{23} atoms, so

$$\left(2.18 \times 10^{-18}\frac{\text{J}}{\text{atom}}\right)\left(6.022 \times 10^{23}\frac{\text{atoms}}{\text{mol}}\right) = 1.31 \times 10^6\ \text{J}$$

Exercise $2.E.47$**

(a) Invalid, the l is equal to the n value.

(b) Invalid, m_l is greater than l.

(c) Invalid, m_l is greater than l.

(d) Allowed.

Exercise $2.E.48$**

Let's first eliminate invalid sets of quantum numbers. a) is not a valid set of quantum numbers because l = n. c) is not a valid set of quantum numbers because l = 1 and m_l = 2 (so that m_l is greater than l).

Magnesium has the electron configuration $1s^2 2s^2 2p^6 3s^2$, so the answer is e). b) describes a 3d orbital and d) a 3p orbital, which are not present in the ground state of Mg.

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3: BONDING AND INTERMOLECULAR FORCES

3.1: Introduction

3.2: Chemical Bonds

3.3: Ionic Bonding

3.4: Covalent Bonding

3.5: Lewis Structures

3.6: Molecular Structure and Polarity

3.7: Intermolecular Forces

3.E: Bonding and Intermolecular Forces (Exercises)

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3.1: Introduction

From Lab Bench to Body Armor: The Story of Kevlar

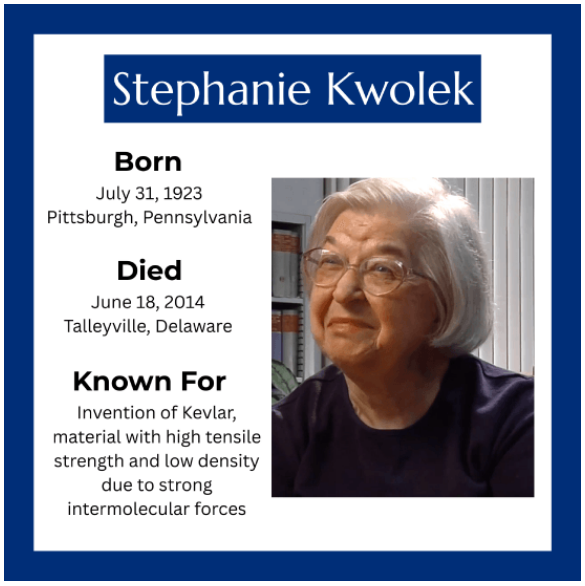


Figure 3.1.1**:** A graphic with basic facts about Stephanie Kwolek, Polish-American chemist who invented the polymer Kevlar. Since her initial discovery, many derivatives of Kevlar have been created with over 200 total applications. The most well-known application is in ballistics protection. Image from Wikimedia Commons, with permission under Creative Commons license CC-BY.

In this chapter, we examine the forces that hold atoms and molecules together. These include intramolecular forces (like covalent bonds) and intermolecular forces (like hydrogen bonding and dispersion forces). The type and strength of these intermolecular interactions help explain important physical properties, such as boiling point, melting point, and whether a substance is a solid, liquid, or gas. For example, water is a liquid at room temperature due to strong hydrogen bonding, while nitrogen is a gas because N_2 molecules interact only weakly.

While these ideas may seem theoretical, they have powerful real-world applications. Chemists use their understanding of bonding and intermolecular forces to design new materials. For example, did you know that Kevlar was created by a chemist?

We've all seen Kevlar vests, whether in person, on the news, or in a TV show, but most people don't realize this remarkable material was only discovered in 1964 by Polish-American chemist Stephanie Kwolek.



Figure 3.1.2**:** A Kevlar vest, commonly used by law enforcement and military for protection from projectiles. The vest is made from fibers Kevlar polymer invented by Stephanie Kwolek. Image from Wikimedia Commons, with permission under Creative Commons license C(

Working for DuPont, Kwolek was trying to develop strong, lightweight fibres for car tires. During her research, she worked with long-chain molecules called polymers that behaved unusually in solution: the molecules lined up in an ordered way, forming what's called a liquid crystal. At the time, this was surprising because most solutions are uniform and disordered.

The lab technician working with Kwolek was reluctant to process the solution through the spinneret (a device that pushes liquid through tiny holes to form solid fibres, like a showerhead for polymers), fearing it would clog the equipment. But Kwolek convinced him to try. To everyone's surprise, the solution spun easily and produced a fibre that was much stronger and more resistant to breaking than nylon.

Kevlar has a tensile strength of 3629 MPa, compared to about 150 MPa for human hair and 250 MPa for A36 steel, which is commonly used in construction. This exceptional strength comes from the interactions between the long chains of molecules, called polymers, that make up the material. In most synthetic polymers at the time, the chains were held together mainly by dispersion forces (weak, temporary attractions) and relied on long chain lengths to build strength. Kevlar is different: each repeating unit (monomer) can form four hydrogen bonds, which are the strongest type of intermolecular force you'll learn about in this chapter. In addition, the benzene rings in the polymer backbone allow for $\pi - \pi$ stacking, an attractive interaction between the flat ring structures on neighbouring strands (see Figure 3). Together, these forces give Kevlar its remarkable strength.

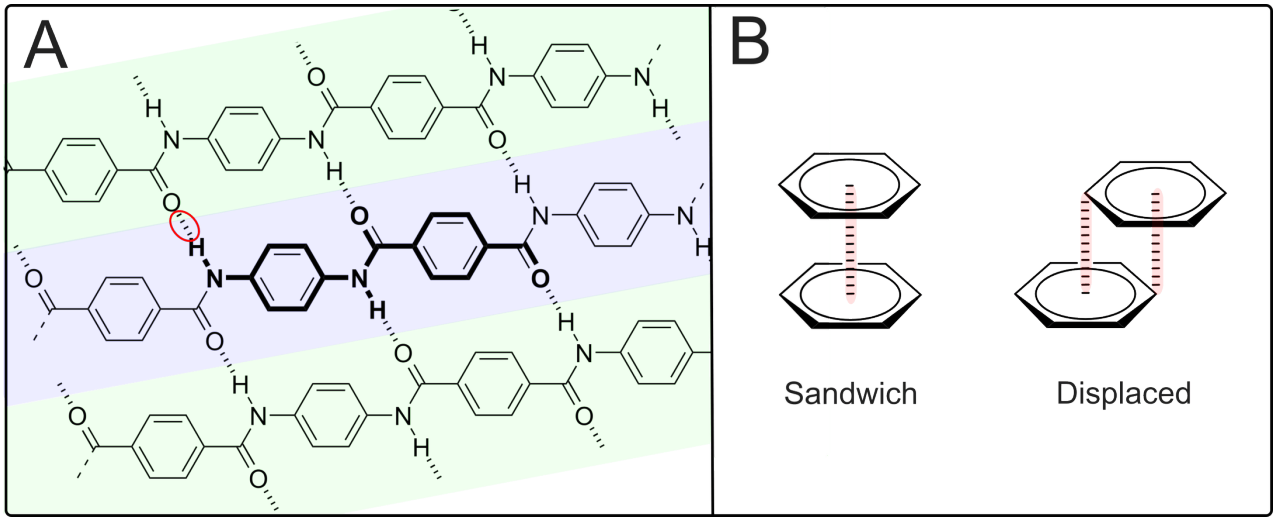


Figure 3.1.3**:** The structure of Kevlar (A). The monomer unit is shown in bold, and each chain is shown with a different background col Interchain hydrogen bonding is indicated by dashed lines - one has been circled in red for clarity. Two common types of $\pi - \pi$ stacking, attractive interaction that occurs when aromatic structures overlap each other, are shown in B. Sandwich type or face to face $\pi - \pi$ stacl when the aromatic centers are aligned for orbital overlap and displaced is when the centers are slightly offset. The interactions are sh with dashed lines, highlighted in pink for clarity.

Not only is Kevlar extremely strong, but it is also very lightweight, with its density only slightly higher than that of human hair. Kwolek's discovery launched a new era in polymer chemistry. Kevlar is now used in more than 200 applications, from bridge cables and tennis rackets to cut-resistant gloves, fiber optics, and, of course, ballistic protection. In this chapter, you'll learn about the types of bonding and intermolecular forces that give materials like Kevlar the strength to stop a bullet, despite being incredibly lightweight.

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3.2: Chemical Bonds

Types of Chemical Bonds

What causes atoms to form bonds with other atoms, rather than remain as individual atoms? The short answer is that bonding lowers the energy of a system, making compounds more stable than isolated atoms. Atoms bond by gaining, losing, or sharing electrons, leading to different types of chemical bonds.

There are three idealized types of bonding, which differ based on how electrons interact between atoms:

1. Ionic bonding occurs when positively and negatively charged ions are held together by electrostatic forces. This type of bonding commonly occurs between metals and nonmetals. To produce the ions involved in the ionic bond, their neutral atoms would have to gain electrons (negative ions) or lose electrons (positive ions), however that process is not necessarily part of forming the ionic bond and could have happened in a previous reaction.
2. Covalent bonding occurs when electrons are shared between atoms in a molecule or a polyatomic ion. This type of bonding occurs most often between nonmetals.
3. Metallic bonding occurs when valence electrons are delocalized across many atoms in a metal, forming a "sea of electrons" that allows metals to conduct electricity and be malleable.

Although we categorize these as three distinct types, bonding exists on a continuum. Some bonds have both ionic and covalent character, depending on the degree of electron sharing or transfer.

Next, we will explore ionic bonding, which occurs when a metal donates one or more electrons to a nonmetal, forming oppositely charged ions.

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3.3: Ionic Bonding

Learning Objectives

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

Atoms gain or lose electrons to form charged particles called ions. A cation is a positively charged ion that forms when an atom loses electrons, while an anion is a negatively charged ion that forms when an atom gains electrons. Because opposite charges attract, these ions do not remain isolated but instead combine to form ionic compounds, held together by strong electrostatic forces called ionic bonds. The formation of an ionic compound releases energy, making the system more stable than the separate ions.

The strong attraction between ions governs the properties of ionic compounds. Ionic solids are hard and brittle due to the fixed arrangement of ions. They also have high melting and boiling points because breaking ionic bonds requires a significant amount of energy. In the solid state, ionic compounds are poor conductors of electricity, but once dissolved or melted, they become excellent electrolytes because the ions can move 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, $\mathrm{Cl_2}$, 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 $3.3.1$). 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 $3.3.1$: (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, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Metallic elements, found to the left in a period or near the bottom of a group on the periodic table, lose electrons relatively easily. Nonmetal atoms, in the upper-right corner of the periodic table, have relatively high electron affinities and thus readily accept electrons lost by metal atoms, filling their valence shells.

When these oppositely charged ions form, they combine in specific ratios to maintain electrical neutrality. The total number

of positive charges from the cations must equal the total number of negative charges from the anions, resulting in a neutral compound. 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, aluminum (Al) forms Al^{3+} cations by losing three electrons, while oxygen (O) forms O^{2-} anions by gaining two electrons. To maintain charge balance, we need enough Al^{3+} cations to cancel out the total negative charge from O^{2-} anions. The simplest ratio is two Al^{3+} ions (2 × +3 = +6) and three O^{2-} ions (3 × –2 = –6), which sum to zero, giving the formula $\mathrm{Al_2O_3}$.

The formula of an ionic compound does not describe its physical structure, only the simplest ratio of ions. Because ionic bonds attract in all directions, ionic compounds do not form discrete molecules, but instead arrange themselves into large, repeating lattice structures. For example, sodium chloride (NaCl) is not a single NaCl pair, but rather a continuous crystal lattice of Na^+ cations and Cl^- anions arranged in a stable, repeating pattern (Figure 3.3.2). This strong electrostatic attraction is what holds the ions tightly together in solid NaCl.

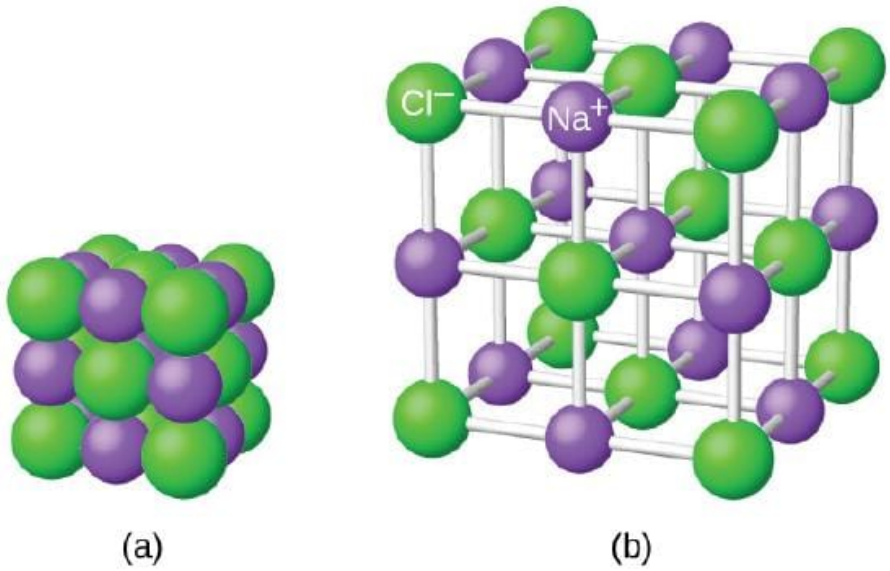


Figure 3.3.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions and the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

Electronic Structures of Cations

Metals tend to lose all their valence electrons to form positively charged cations with the same electron configuration as the nearest noble gas. For example, calcium (Z=20) has the electron configuration $[\mathrm{Ar}]4s^2$. When it loses its two valence electrons, it forms Ca^{2+}, which is isoelectronic with argon.

Example 3.3.1: Determining the Electronic Structures of Cations

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected to form from these elements.

Solution

Consider the electron configuration of the atoms:

K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

K can lose one electron to have a filled valence shell. K^+ has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$ which is the same as $[\mathrm{Ar}]$

Mg $1s^2 2s^2 2p^6 3s^2$

Mg can lose two electrons to have a filled valence shell. Mg^{2+} has the electron configuration $1s^2 2s^2 2p^6$ which is the same as $[\mathrm{Ne}]$

Electronic Structures of Anions

Nonmetals tend to gain electrons to fill their valence shell, forming negatively charged anions. For example, oxygen (Z=8) has the electron configuration $[\mathrm{He}]2s^2 2p^4$. To reach a full octet, it gains two electrons, forming O^{2-}, which is isoelectronic with neon.

Example 3.3.2: Determining the Electronic Structure of Anions

Selenium (Se) and iodine (I) are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Consider the electron configuration of the atoms:

Se $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

Se can gain two electrons to have a filled valence shell. Se^{2-} has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ which is the same as $[\mathrm{Kr}]$

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

I can gain one electron to have a filled valence shell. I^- has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ which is the same as $[\mathrm{Se}]$

Exercise 3.3.1

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer available at the end of this section.

Summary

Ionic bonds form due to the electrostatic attraction between metallic cations and nonmetallic anions. Because these forces act in all directions, ionic compounds arrange into a lattice structure rather than forming discrete molecules. Cations tend to lose valence electrons to achieve a more stable electron configuration, often resembling a noble gas. Anions tend to gain electrons to fill their valence shell. The strong ionic bonds give these compounds high melting points, brittleness, and the ability to conduct electricity when dissolved or molten.

Glossary

binary ionic compound
: An ionic compound containing two different elements, one metal and one nonmetal.

ionic compound
: A compound composed of cations and anions combined in ratios, yielding an electrically neutral substance.

ionic solid
: A solid composed of positive and negative ions held together by strong electrostatic attractions.

Answers

Exercise 3.3.1

P: [Ne]$3s^2 3p^3$; P^{3-}: [Ar]

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3.4: Covalent Bonding

Learning Objectives

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

Ionic bonds form due to the electrostatic attraction between oppositely charged ions, typically after electrons are transferred between a metal and a nonmetal. In contrast, covalent bonds form when two atoms share a pair of electrons, rather than transferring them. This happens when both atoms have similar tendencies to attract electrons. For example, in an $\mathrm{H_2}$ molecule, two hydrogen atoms share their electrons, so that each achieves the same number of valence electrons as helium (He), a noble gas.

Covalent compounds have distinct physical properties compared to ionic compounds. Ionic compounds have high melting and boiling points because breaking ionic bonds requires a large amount of energy. In contrast, covalent compounds tend to have much lower melting and boiling points because, when they change state (from solid to liquid, or liquid to gas), the bonds between atoms remain intact—only the weaker attractions between molecules are disrupted. Many covalent compounds are liquids or gases at room temperature. Unlike ionic compounds, which conduct electricity when dissolved in water, most covalent compounds do not dissolve in water and are poor conductors of electricity.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. Why is this the case? For example, the hydrogen molecule, $\mathrm{H_2}$, contains a covalent bond between its two hydrogen atoms. Figure $3.4.1$ shows a plot of the potential energy for two hydrogen atoms as the distance between their nuclei changes.

Starting on the far right of the graph, the potential energy of two separate hydrogen atoms is indicated by the red line. At this point, the hydrogen atoms are too far apart to interact. As the two atoms approach each other (moving left along the *x*-axis), the electron of one hydrogen atom is attracted to the nucleus of the other hydrogen atom and vice versa (opposite charges attract!). The attraction of each electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases.

However, as the atoms move closer together, the positive charges in the two nuclei begin to repel each other, causing the potential energy to increase. A covalent bond forms when the attraction between each nucleus and the shared electrons outweighs the repulsion between the two positively charged nuclei. The bond length is the distance at which the system reaches its lowest energy, maximizing the stability of the molecule.

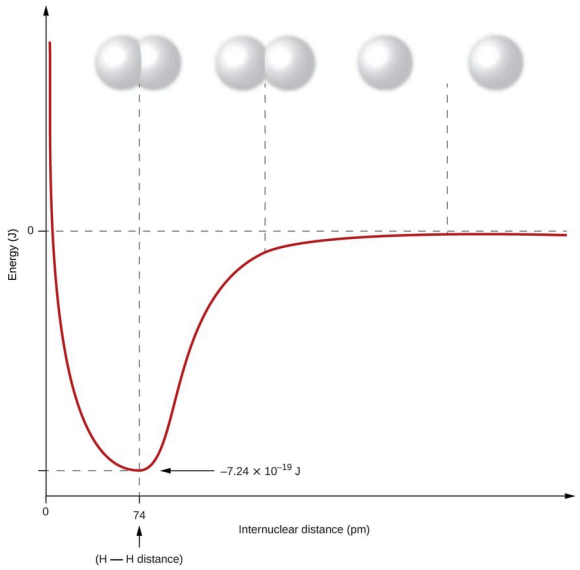


Figure 3.4.1: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

Breaking a chemical bond requires energy (an endothermic process), while forming a bond releases energy (an exothermic process). The $\mathrm{H_2}$ covalent bond is strong. As shown in Figure 3.4.1, breaking a single $\mathrm{H{-}H}$ bond requires 7.2 x 10^{-19} J, while breaking one mole of $\mathrm{H_2}$ molecules requires 436 kJ.

$$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(g)} \quad \Delta H = 436\,\mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of $\mathrm{H_2}$ molecules forms from two moles of H atoms:

$$\mathrm{2\,H\,(g)} \longrightarrow \mathrm{H_2\,(g)} \quad \Delta H = -436\,\mathrm{kJ}$$

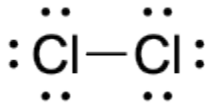
Covalent bonds are electrostatic in nature - they result from the attraction between an atom's positively charged nucleus and the negatively charged electrons of another atom.

Pure vs. Polar Covalent Bonds

When two identical atoms form a covalent bond—such as in $\mathrm{H_2}$, $\mathrm{Cl_2}$, and other diatomic molecules—the electrons are shared equally. This is called a nonpolar or pure covalent bond. In pure covalent bonds, electrons spend equal time near each nucleus.

For example, in a $\mathrm{Cl_2}$ molecule, each chlorine atom has seven valence electrons. By sharing one electron with the other chlorine atom, they form a single covalent bond: achieving the same number of valence electrons as argon:

$$\mathrm{Cl + Cl \longrightarrow Cl_2}$$



Each atom has six nonbonding electrons (lone pairs) and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since both atoms in the bond are identical, the electron distribution is equal, making $\mathrm{Cl_2}$ a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but not necessarily equally. Instead, the bonding electrons can be 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 has a partial negative charge

(the atom is getting more than half of the electron density), while the atom that attracts the electrons less strongly has a partial positive charge (the atom is getting less than half of the electron density).

For example, the electrons in the $\mathrm{H{-}Cl}$ 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 $3.4.2$ shows the distribution of electrons in the $\mathrm{H{-}Cl}$ bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure $3.4.1$, which shows the even distribution of electrons in the $\mathrm{H_2}$ nonpolar bond.

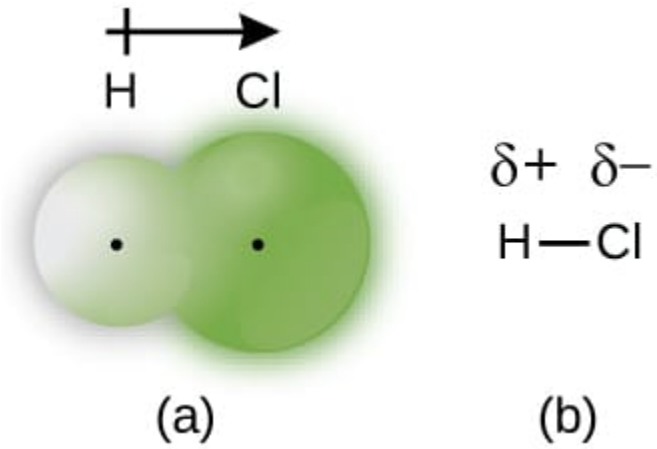


Figure $3.4.2$: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the $\mathrm{H{-}Cl}$ bond.

We can show the unequal sharing of electrons using a polar arrow,  . Notice in Figure $3.4.2$ that the arrow points towards Cl, the partially negative atom. We can also designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the $\mathrm{H{-}Cl}$ molecule in Figure $3.4.2$. Why do electrons in the HCl bond spend more time near Cl rather than being shared equally? This behavior is due to electronegativity, a measure of how strongly an atom attracts electrons in a bond.

Electronegativity

Electronegativity is a measure of how strongly an atom attracts shared electrons in a chemical bond. It determines whether electrons in a bond are shared equally (nonpolar covalent) or unequally (polar covalent). In a polar covalent bond, electrons shift toward the more electronegative atom, giving it a partial negative charge (δ⦰), while the other atom takes on a partial positive charge (δ⦰).

The greater the difference in electronegativity between two atoms, the more unequally the electrons are shared. This creates larger partial charges (δ⦰ and δ⦰) on the atoms, increasing bond polarity.

Figure $3.4.3$ shows the electronegativity values of the elements as proposed by Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Nonmetals, located in the upper right of the periodic table, tend to have the highest electronegativities. Fluorine (EN = 4.0) is the most electronegative element. In contrast, metals have lower electronegativities, with group 1 metals being the least electronegative. Noble gases are typically excluded from electronegativity trends because they have full valence shells and rarely form bonds. However, some noble gas compounds (e.g., $\mathrm{XeO_2}$) can form under extreme conditions, making their electronegativity values less relevant in general trends.

Trends in electronegativity across the periodic table are opposite to those described for atomic radius in Section 2.8. This is because electronegativity and atomic radius are both related the effective nuclear change (Z_{eff}) experienced by the valence electrons, but in opposite ways. Z_{eff} increases across a row as protons are added to the nucleus without any change in the number of inner-core shielding electrons. Increasing Z_{eff} increases the pull of the nucleus on the valence electrons, increases

electronegativity and decreasing atomic radius. Z_{eff} decreases down a column, as electrons occupy orbitals further from the nucleus, decreasing electronegativity and increasing atomic radius.

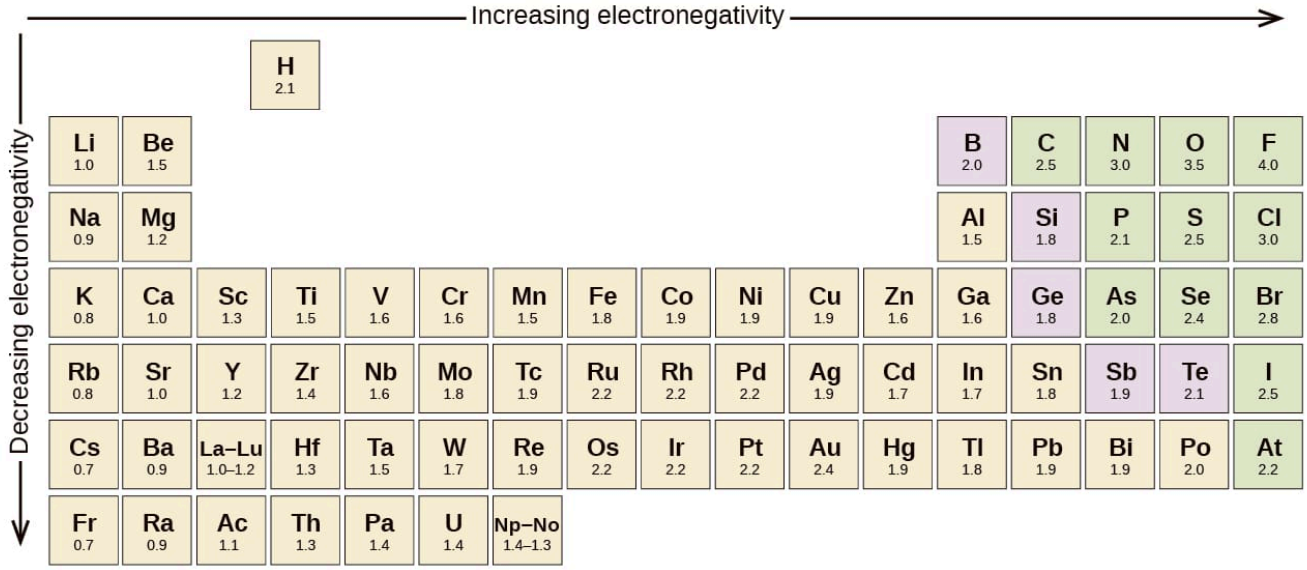


Figure 3.4.3: The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

Electronegativity measures how strongly an atom attracts electrons in a bond. It is a dimensionless, calculated value rather than a directly measured property. Linus Pauling first developed electronegativity values by comparing the bond dissociation energies of different chemical bonds, creating an arbitrary relative scale from 0 to 4.

Portrait of a Chemist: Linus Pauling

Linus Pauling, shown in Figure 3.4.4, 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 3.4.4: 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 difference in electronegativity (ΔEN) between two atoms helps to determine the type of bond they form.

- If ΔEN is small or zero, the bond is nonpolar covalent (electrons are shared equally).
- If ΔEN is moderate, the bond is polar covalent (electrons are shared unevenly).
- If ΔEN is large, the bond is ionic (electrons are transferred, not shared).

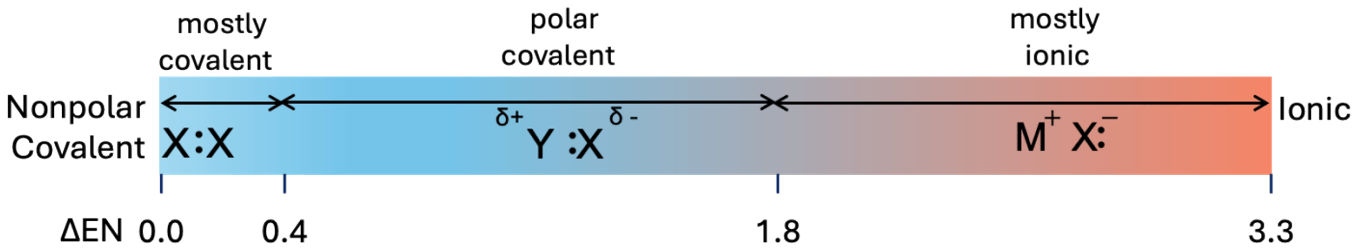


Figure 3.4.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Figure 3.4.5 provides a general guide for classifying bonds based on electronegativity differences, but the difference between these three classifications is a continuum and so there are many exceptions. For example, HF has a ΔEN of 1.9, while $\mathrm{NH_3}$ has a ΔEN of 0.9 and yet both are considered polar covalent. Similarly, NaCl has a ΔEN of 2.1, while $\mathrm{MnI_2}$ has a ΔEN of 1.0, but both form ionic compounds.

Another way to predict bond type is to consider the elements involved and their positions on the periodic table:

- Bonds between two nonmetals are usually covalent.
- Bonds between a metal and a nonmetal are typically ionic.

Some compounds contain both covalent and ionic bonds. Polyatomic ions (e.g., $\mathrm{OH^-}$) have atoms held together by polar covalent bonds, but they form ionic compounds when combined with oppositely charged ions.

For example, potassium nitrate ($\mathrm{KNO_3}$) contains both ionic and covalent bonds. The $\mathrm{K^+}$ cation and $\mathrm{NO_3^-}$ anion are held together by ionic bonds, while the nitrogen and oxygen atoms in $\mathrm{NO_3^-}$ are bonded covalently.

Example 3.4.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Consider the following covalent bonds, all commonly found in amino acids:

a) Using the electronegativity values in Figure 3.4.3, use polar arrows and partial positive and partial negative symbols to indicate the bond polarity.

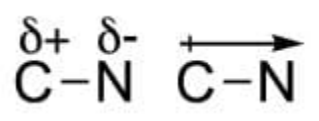
b) Arrange the following covalent bonds in order of increasing polarity.

$$\mathrm{C{-}H,\ C{-}N,\ C{-}O,\ N{-}H,\ O{-}H}$$

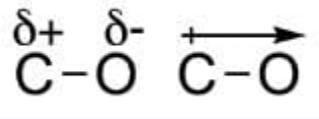
Solution

a) $\mathrm{C{-}H}$: EN of C = 2.5; EN of H = 2.1; ΔEN = 0.4. The difference in electronegativity is small enough that the $\mathrm{C{-}H}$ bond is considered nonpolar.

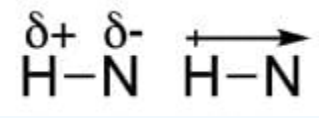
C—N: EN of C = 2.5; EN of N = 3.0; ΔEN = 0.5. The C—N bond is considered polar covalent. The bond polarity can indicated with either partial charges or with the polar arrow:



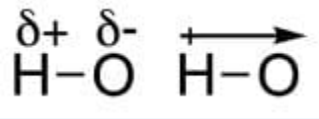
C—O: EN of C = 2.5; EN of O = 3.5; ΔEN = 1.0. The C—O bond is considered polar covalent. The bond polarity can indicated with either partial charges or with the polar arrow:



N—H: EN of N = 3.0; EN of H = 2.1; ΔEN = 0.9. The N—H bond is considered polar covalent. The bond polarity can indicated with either partial charges or with the polar arrow:



O—H: EN of O = 3.5; EN of H = 2.1; ΔEN = 1.4. The O—H bond is considered polar covalent. The bond polarity can indicated with either partial charges or with the polar arrow:



The arrow in all cases points towards the more electronegative element. Alternatively, the more electronegative element is indicated with the δ– since it attracts more electron density and will have a partial negative charge.

b) The polarity of these bonds increases as the absolute value of the electronegativity difference increases:

C—H < C—N < N—H < C—O < O—H

Summary

Covalent bonds form when two atoms share electrons, with each nucleus attracting the shared electrons. In pure covalent bonds, electrons are shared equally between atoms. In polar covalent bonds, one atom pulls the electrons closer, creating an uneven charge distribution.

Electronegativity describes how strongly an atom attracts shared electrons in a bond. The greater the difference in electronegativity, the more polar the bond.

In a diatomic molecule with identical atoms, there is no electronegativity difference, so the bond is nonpolar covalent. When the electronegativity difference is very large—such as between metals and nonmetals—the bond is ionic, meaning electrons are transferred rather than shared.

Glossary

bond distance
: The distance between the nuclei of two bonded atoms, typically measured in Ångstroms or picometers; also called bond length.

covalent compound
A compound composed of molecules formed by atoms of two or more different elements.

electronegativity
The tendency of an atom to attract electrons in a bond to itself.

electrostatic attraction
Attraction between an atom's positively charged nucleus and the negatively charged electrons of another atom.

polar covalent bond
Covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end.

pure covalent bond
Covalent bond between atoms of identical electronegativities; also called a nonpolar covalent bond.

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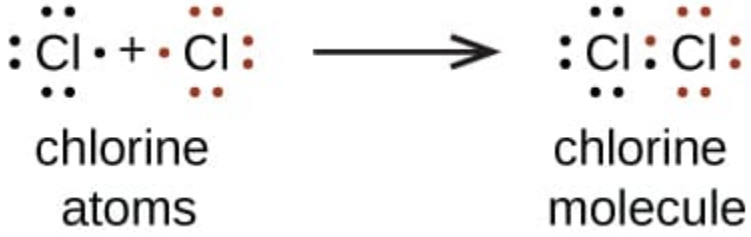
3.5: Lewis Structures

Learning Objectives

- Draw Lewis structures depicting the bonding in simple molecules

So far in this chapter, we have discussed types of bonds that form between atoms and/or ions. These bonds involve either the sharing or transfer of valence electrons between atoms. In this section, we will explore a common method for depicting valence shell electrons in molecules, namely Lewis structures. Lewis structures show the placement of atoms in a molecule or polyatomic ion and the distribution of valence electrons in bonds and lone pairs. Lewis structures are based on the idea that atoms share electrons in a bond to complete their valence shell (often an octet or 8 electrons to fill the s and p orbitals). Lewis structures give us a simplified picture of bonding that helps us predict the arrangement of electrons in molecules.

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 typically used to indicate a shared pair of electrons:

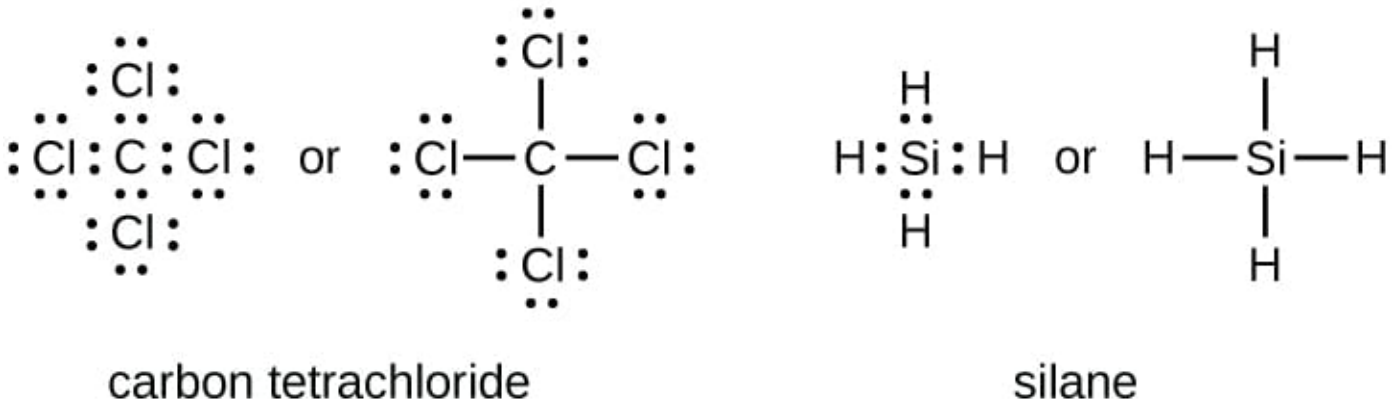


A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two shared in the single bond.

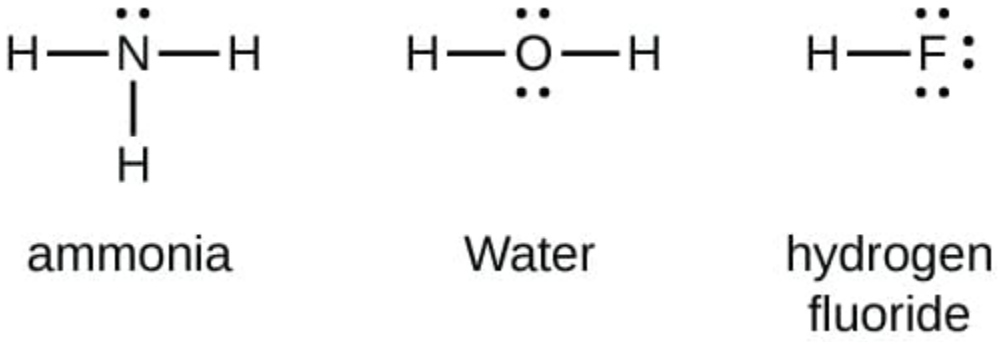
The Octet Rule

The other halogen molecules ($\mathrm{F_2}$, $\mathrm{Br_2}$, $\mathrm{I_2}$, and $\mathrm{At_2}$) 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. However, some molecules do not follow this rule, which we will explore later.

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 $\mathrm{CCl_4}$ (carbon tetrachloride) and silicon in $\mathrm{SiH_4}$ (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.

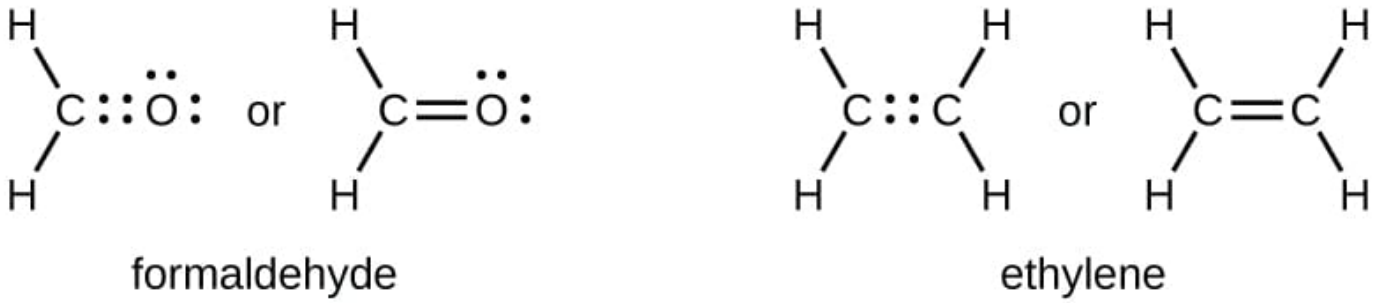


Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in $\mathrm{NH_3}$ (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in $\mathrm{CH_2O}$ (formaldehyde) and between the two carbon atoms in $\mathrm{C_2H_4}$ (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 ($\mathrm{CN^-}$):



Writing Lewis Structures with the Octet Rule

The step-by-step procedure outlined for writing Lewis structures is described below:

Writing Lewis Structures

1. Determine the total number of valence (outer shell) electrons. For ions, add an electron for each negative charge and subtract one electron for each positive 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). Subtract two electrons from the total for each bond.
3. Distribute the remaining electrons as lone pairs, completing an octet, 8 electrons, around each outer atom. Subtract the lone pair electrons from the remaining electrons.
4. Place all remaining electrons as lone pairs on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom to obtain octets wherever possible.

Let us determine the Lewis structures of $\mathrm{SiH_4}$, $\mathrm{CHO_2^-}$, and $\mathrm{OF_2}$ as examples of using this procedure.

Example 3.5.1

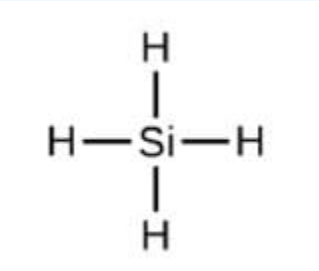
Draw the Lewis structure for $\mathrm{SiH_4}$.

Solution

1. Determine the total number of valence (outer shell) electrons.

$$\begin{aligned} & & \mathrm{SiH_4} \\ & \text{Si: 4 valence electrons/atom} \times \ 1 \text{ atom} \ &= 4 \\ + \quad & \text{H : 1 valence electron/atom} \times \ 4 \text{ atoms} &= 4 \\ & \text{total valence electrons} &= 8 \end{aligned}$$

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). Subtract two electrons for each bond.



8 electrons - 8 bonding electrons = 0 electrons left

Si has an octet and each H has 2 electrons, so the Lewis structure is complete.

Example 3.5.2

Draw the Lewis structure for $\mathrm{CHO_2}^-$.

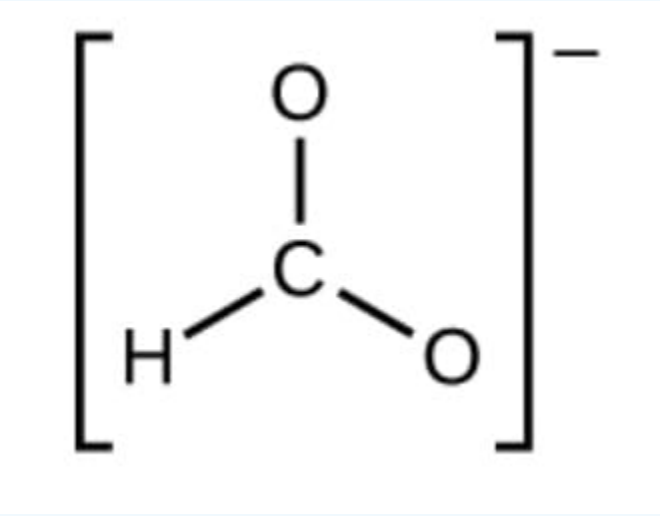
Solution

1. Determine the total number of valence (outer shell) electrons.

For a *negative ion*, such as $\mathrm{CHO_2}^-$, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{aligned} & & \mathrm{CHO_2}^- \\ \mathrm{C}\text{: } 4 \text{ valence electrons/atom} \times & \ 1 \text{ atom} & = 4 \\ \mathrm{H}\text{: } 1 \text{ valence electron/atom} \times & \ 1 \text{ atoms} & = 1 \\ \mathrm{O}\text{: } 6 \text{ valence electron/atom} \times & \ 2 \text{ atoms} & = 12 \\ + & 1 \text{ electron} & = 1 \\ & \text{total valence electrons} & = 18 \end{aligned}$$

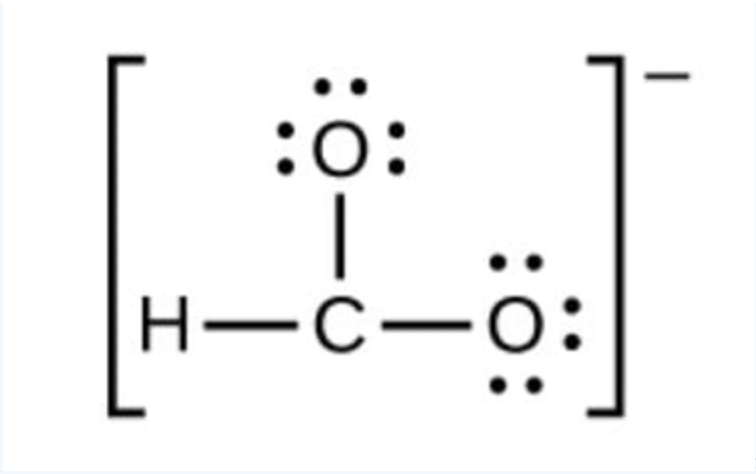
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. Generally, the least electronegative element should be placed in the center. Connect each atom to the central atom with a single bond (one electron pair). (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



Subtract two electrons for each bond:

18 electrons - 6 bonding electrons = 12 electrons left

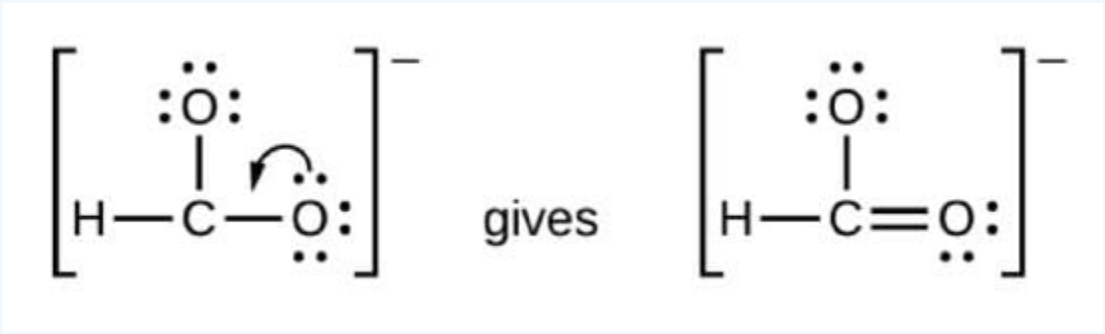
3. Distribute the remaining electrons as lone pairs, completing an octet, 8 electrons, around each outer atom. Subtract the lone pair electrons from the remaining electrons.



Since H can only have 2 electrons, it cannot have a lone pair.

12 electrons - 12 electrons = 0 electrons left. Since there are no electrons remaining, we skip to step 5.

5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible:



Moving one lone pair to form a double bond gives the central C 8 shared electrons.

Example 3.5.3

Draw the Lewis structure for $\mathrm{OF_2}$.

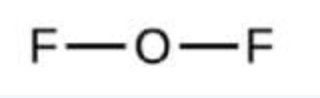
Solution

1. Determine the total number of valence (outer shell) electrons.

Since $\mathrm{OF_2}$ is a neutral molecule, we simply add the number of valence electrons:

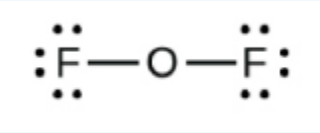
$$\begin{aligned} & \mathrm{OF_2} \\ \mathrm{O}\text{: } 6 \text{ valence electrons/atom} \times & \ 1 \text{ atom} \ = 6 \\ + \quad \mathrm{F}\text{: } 7 \text{ valence electron/atom} \times & \ 2 \text{ atoms} = 14 \\ & \text{total valence electrons} = 20 \end{aligned}$$

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).



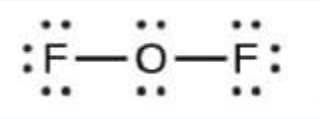
Subtract two electrons for each bond. 20 electrons - 4 bonding electrons = 16 electrons left

3. Distribute the remaining electrons as lone pairs, completing an octet, 8 electrons, around each outer atom. Subtract the lone pair electrons from the remaining electrons.



16 electrons - 12 lone pair electrons = 4 electrons left.

4. Place all remaining electrons as lone pairs on the central atom.



The atoms each have 8 electrons, so the Lewis structure is complete.

Example 3.5.4: Writing Lewis Structures

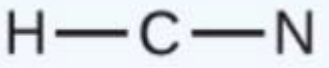
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. What is the Lewis structure of HCN?

Solution

Step 1. *Calculate the number of valence electrons.*

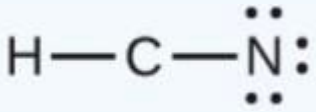
HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10

Step 2 *Draw a skeleton and connect the atoms with single bonds*. Remember that H is never a central atom:



10 electrons - 4 bonding electrons = 6 electrons left

Step 3. *Distribute electrons to the terminal atoms:*

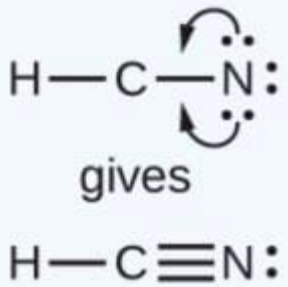


6 electrons - 6 lone pair electrons = 0 electrons left

Step 4. *There are no remaining electrons and* C *does not have an octet so we can move on to Step 5.*

Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

Carbon is only sharing 4 electrons, so it needs to share two more pairs of electrons to have 8 electrons. Two lone pairs can be rearranged to form a triple bond between C and N.



Exercise 3.5.1

Both carbon monoxide, CO, and carbon dioxide, $\mathrm{CO_2}$, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and $\mathrm{CO_2}$ has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer available at the end of this section.

How Sciences Interconnect: Fullerene Chemistry

Carbon, in various forms and compounds, has been known since prehistoric times. Soot has been used as a pigment (often called carbon black) for thousands of years. Charcoal, high in carbon content, has likewise been critical to human development. Carbon is the key additive to iron in the steel-making process, and diamonds have a unique place in both culture and industry. Significant research into carbon, particularly with the emergence of organic chemistry, led to the discovery of even more varied and extensive carbon structures.

As early as the 1960s, chemists began to observe complex carbon structures, but they had little evidence to support their concepts, or their work did not make it into the mainstream. Eiji Osawa predicted a spherical form based on observations of a similar structure, but his work was not widely known outside Japan. In a similar manner, the most comprehensive advance was likely computational chemist Elena Galpern's, who in 1973 predicted a highly stable, 60-carbon molecule; her work was also isolated to her native Russia. Still later, Harold Kroto, working with Canadian radio astronomers, sought to uncover the nature of long carbon chains that had been discovered in interstellar space.

Kroto sought to use a machine developed by Richard Smalley's team at Rice University to learn more about these structures. Together with Robert Curl, who had introduced them, and three graduate students—James Heath, Sean O'Brien, and Yuan Liu—they performed an intensive series of experiments that led to a major discovery.

In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 3.5.3), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the $\mathrm{C_{60}}$ buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on $\mathrm{C_{60}}$. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

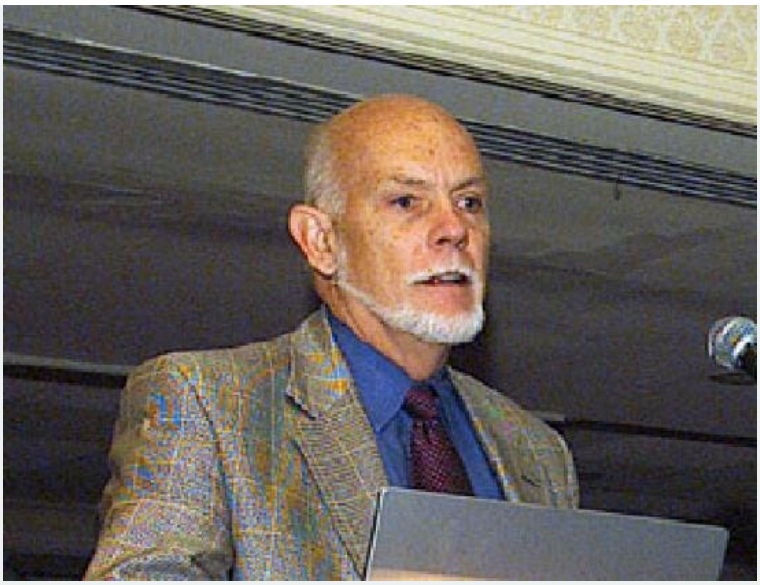


Figure 3.5.1: Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

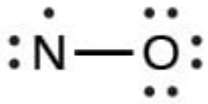
- Odd-electron molecules have an odd number of valence electrons and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

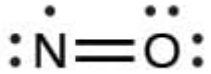
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an $\mathrm{N}-\mathrm{O}$ single bond:
   $\mathrm{N}-\mathrm{O}$
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:



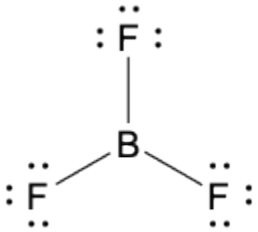
4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible*. We know that an odd-electron molecule cannot have an octet for 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:)

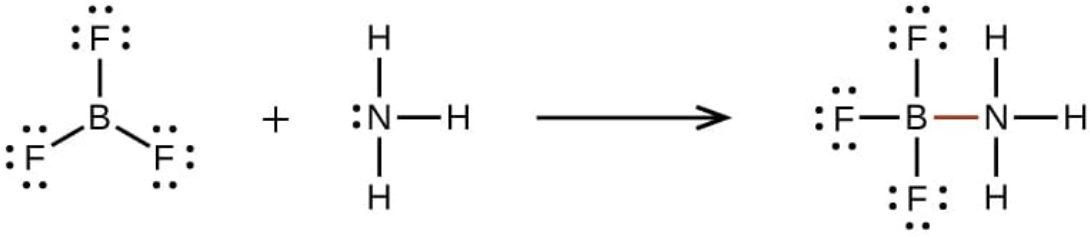


Electron-deficient Molecules

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 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of boron trifluoride, $\mathrm{BF_3}$, the boron atom has only six electrons. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in $\mathrm{BF_3}$, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for $\mathrm{B{-}F}$ single bonds. This suggests the best Lewis structure has three $\mathrm{B{-}F}$ single bonds and an electron-deficient boron. The reactivity of the compound is also consistent with an electron-deficient boron. However, the $\mathrm{B{-}F}$ bonds are slightly shorter than expected for $\mathrm{B{-}F}$ single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in $\mathrm{BF_3}$, 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, $\mathrm{NF_3}$ reacts with $\mathrm{BF_3}$ 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 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figure $3.5.4$: shows the Lewis structures for two hypervalent molecules, $\mathrm{PCl_5}$ and $\mathrm{SF_6}$.

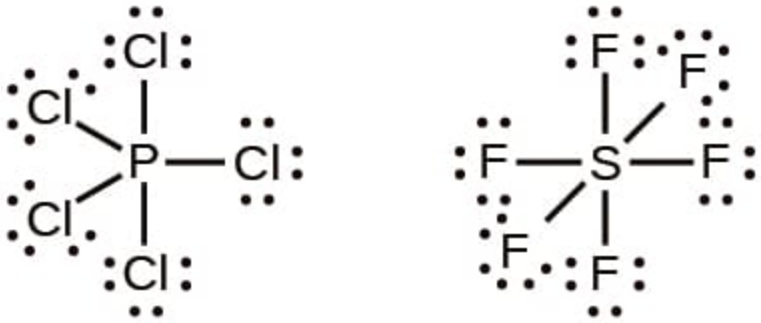
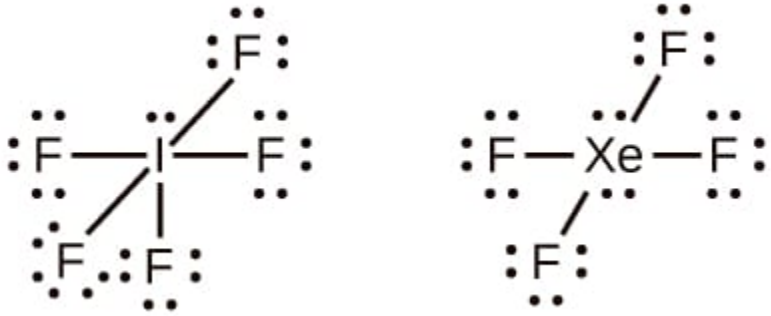


Figure 3.5.2: In $\mathrm{PCl_5}$, the central atom phosphorus shares five pairs of electrons. In $\mathrm{SF_6}$, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as $\mathrm{IF_5}$ and $\mathrm{XeF_4}$, 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 3.5.5: Writing Lewis Structures - Octet Rule Violations

Xenon is a noble gas, but it forms some stable compounds. We examined $\mathrm{XeF_4}$ earlier. What are the Lewis structures of $\mathrm{XeF_2}$ and $\mathrm{XeF_6}$?

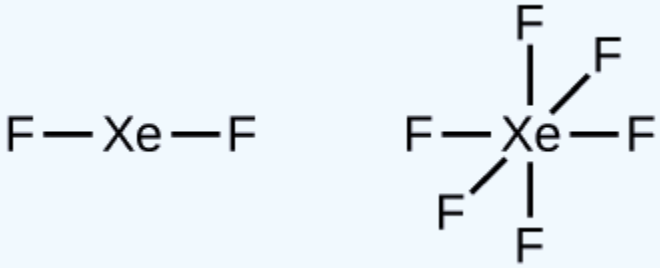
Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

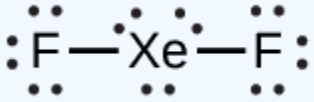
$\mathrm{XeF_2}$: 8 + (2 × 7) = 22
$\mathrm{XeF_6}$: 8 + (6 × 7) = 50

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

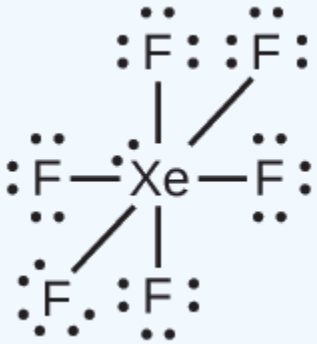


Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 3.5.2: Interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Answer available at the end of this section.

Looking Forward to CHM 136

We will not be covering formal charge and resonance as it is part of the CHM 136H curriculum. This section is included in case you want to look ahead or refer to it next semester during CHM 136H.

We learned how to write Lewis structures for molecules and polyatomic ions. Sometimes, there can be more than one valid structure for a molecule. We use formal charges to predict the most suitable Lewis structure in such cases.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the non-bonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge } = \#\text{ valence shell electrons (free atom)} - \#\text{ lone pair electrons } - \frac{1}{2}\#\text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

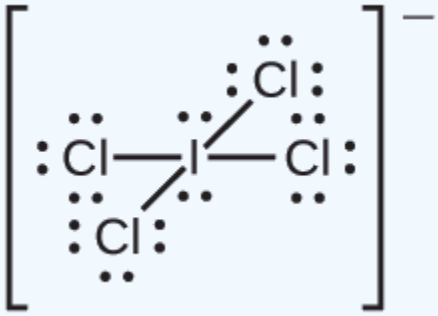
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 3.5.6: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in $\mathrm{ICl_4^-}$.

Solution

Step 1. Draw the Lewis structure for the ion, making sure to include lone pairs.



Step 2. Calculate the formal charge for each atom:

I: 7 valence electrons - 1/2(8 bonding electrons) - 4 lone pair electrons = -1

More conceptually, we can consider that in the molecule, I has 4 lone pair electrons and contributes 1 electron to each bond, for a total of 8 electrons in the molecule. Since this is one more than the number of valence electrons, the formal charge is -1.

All of the Cl atoms are the same. Cl: 7 valence electrons - 1/2(2 bonding electrons) - 6 lone pair electrons = 0

More conceptually, we can consider that in the molecule, each Cl has 6 lone pair electrons and contributes 1 electron to the $\mathrm{I{-}Cl}$ bond, for a total of 7 electrons in the molecule. Since Cl has 7 valence electrons, the formal charge for each $\mathrm{I{-}Cl}$ is 0.

Step 3. Check that the sum of the formal charges equals the charge of the ion: -1 + 0 + 0 + 0 + 0 = -1

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Exercise 3.5.3

Calculate the formal charge for each atom in the carbon monoxide molecule:



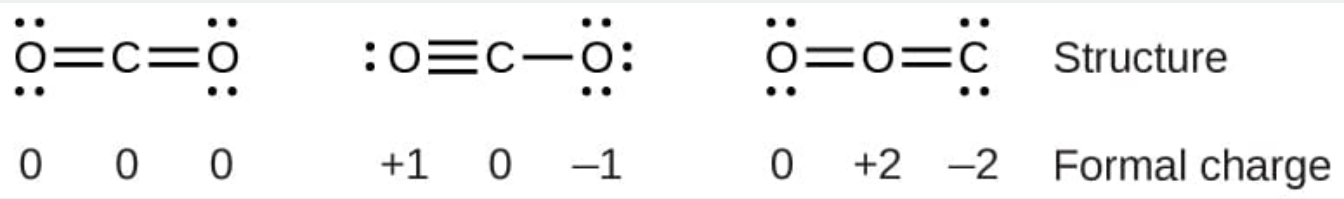
Answer available at the end of this section.

Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is its molecular structure. Writing Lewis structures can sometimes result in multiple possible structures, with different bond and lone pair placements or atom arrangements. Guidelines involving formal charge help determine the most likely structure:

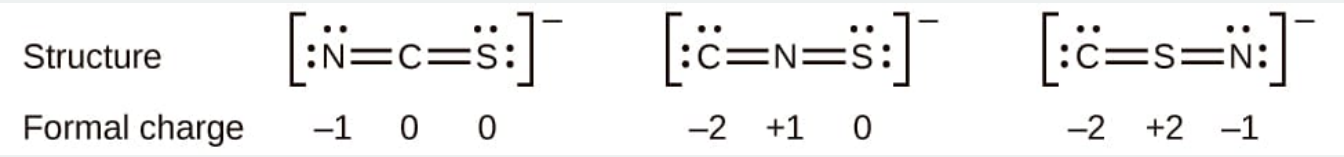
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, $\mathrm{CO_2}$ We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

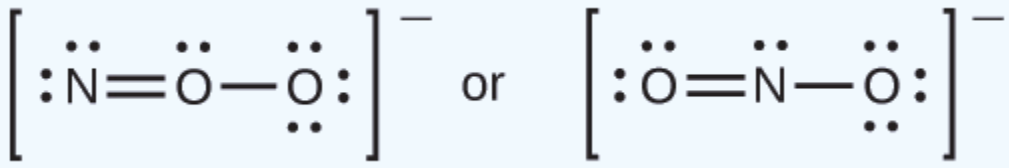
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: $\mathrm{NCS^-}$, $\mathrm{CNS^-}$, or $\mathrm{CSN^-}$. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Exercise 3.5.4

Which is the most likely molecular structure for the nitrite ion?



Answer available at the end of this section.

Resonance

Some molecules or ions have structures that cannot be adequately shown with a single representation. For example, the nitrite anion could be drawn in two different ways, distinguished by the locations of the $\mathrm{N{-}O}$ and $\mathrm{N{=}O}$ bonds:



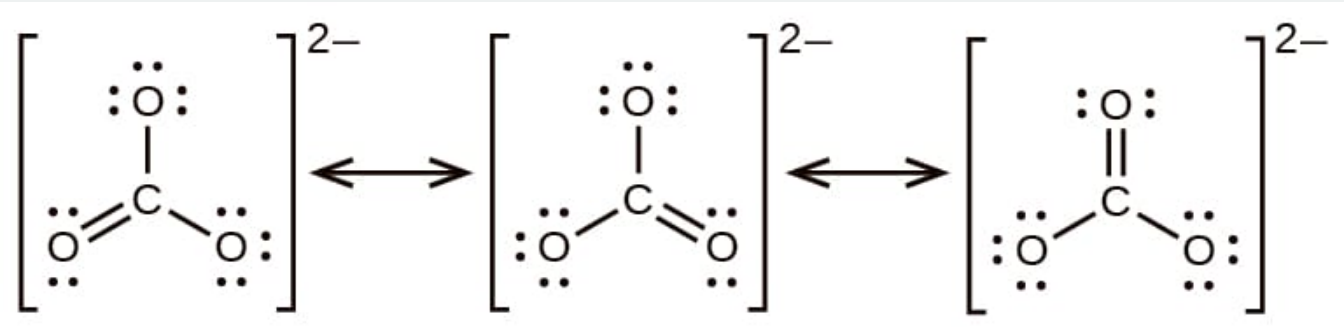
If nitrite ions had a single and a double bond, the bond lengths would differ, with the double bond being shorter and stronger. However, experiments show that both $\mathrm{N{-}O}$ bonds in the nitrite ion are identical in length, strength, and other properties.

It is not possible to write a single Lewis structure in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three $\mathrm{C{-}O}$ bonds are the same.

Summary

Lewis structures represent valence electron arrangements using Lewis symbols for atoms and monatomic ions and Lewis structures for molecules and polyatomic ions. They use lone pairs, unpaired electrons, and single, double, or triple bonds to show how valence electrons are distributed around each atom. Most molecules, especially those with second-row elements, follow the octet rule, where atoms (except hydrogen) are surrounded by eight electrons. However, some molecules do not follow this rule. Exceptions include odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Glossary

double bond
A bond in which two pairs of electrons are shared between two atoms.

electron-deficient molecule
A molecule containing a central atom without a filled valence shell.

free radical
A molecule that contains an odd number of electrons.

hypervalent molecule
A 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.

lone pair
Two (a pair of) valence electrons that are not used to form a 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
A bond in which a single pair of electrons is shared between two atoms.

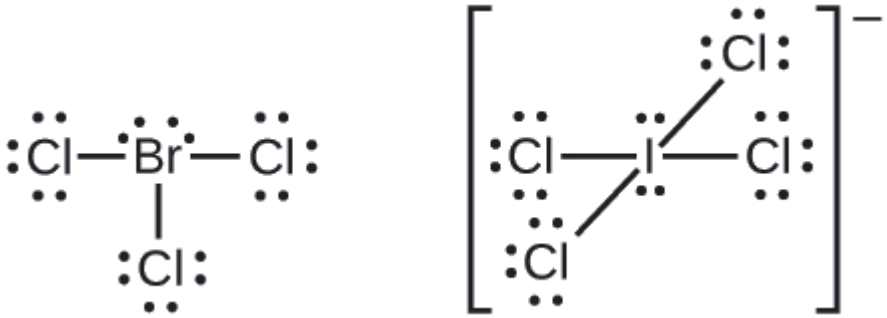
triple bond
A bond in which three pairs of electrons are shared between two atoms.

Answers

Exercise 3.5.1



Exercise 3.5.2**: Interhalogens**



Exercise 3.5.3

\(\ce{C}\) –1, \(\ce{O}\) +1

Exercise 3.5.4

ONO

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3.6: Molecular Structure and Polarity

Learning Objectives

- 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

So far, we have used two-dimensional Lewis structures to represent molecules. However, molecules exist in three dimensions, and their shapes influence their properties and behaviour. Molecular structure can be described using bond distances, bond angles, and relative arrangements in space (Figure 3.6.1). A bond angle is the angle between two bonds that share an atom, measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms, typically measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

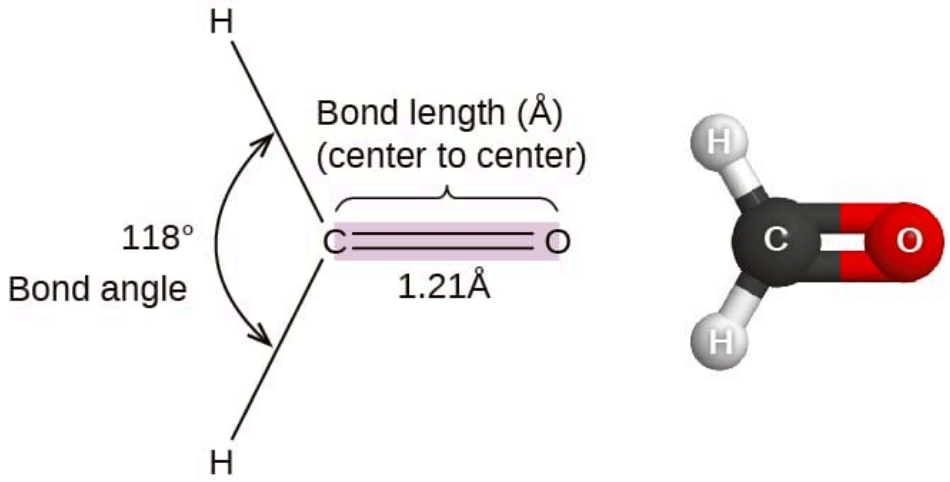


Figure 3.6.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence Shell Electron-Pair Repulsion (VSEPR) theory is a model that helps predict molecular shape, including bond angles around a central atom. It does this by considering the number of electron groups—regions of electron density—around the central atom in a Lewis structure.

An electron group can be:

- A lone pair
- A single, double, or triple bond (each counts as one electron group)

Since bonding electrons are shared in the same region of space, multiple bonds count as one group in VSEPR theory.

The VSEPR model assumes that electron groups repel each other and arrange themselves as far apart as possible to minimize repulsions. While VSEPR has limitations and does not always predict shapes of complex molecules, it is very useful for simple molecules.

To see how VSEPR works, let's look at carbon dioxide (CO_2). The Lewis structure of CO_2 (Figure 3.6.2) shows two bonds and no lone pairs around the central carbon atom. Since each double bond counts as one electron group, there are two electron groups in total. These electron groups repel each other and spread out as far apart as possible, creating a linear shape with a bond angle of 180°.

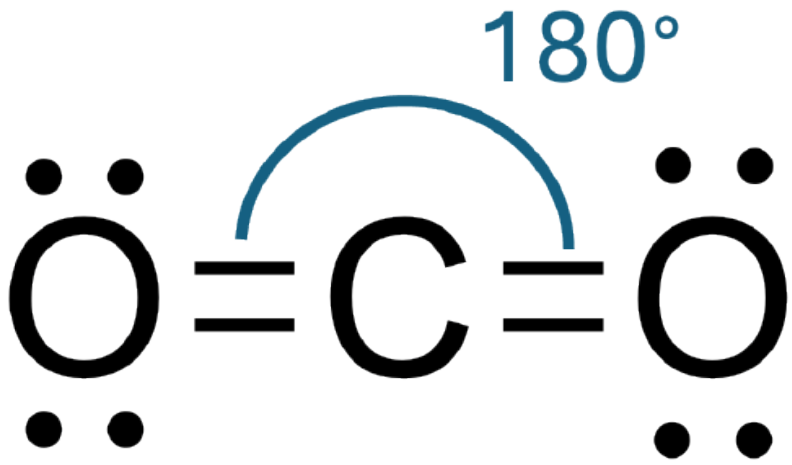


Figure 3.6.2: The CO_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the C atom.

Figure 3.6.3 shows molecular shapes arranged by the number of electron groups.

Two electron groups (regions of electron density around a central atom) give a linear geometry with an ideal bond angle of 180°.

Three electron groups give a trigonal planar geometry with all atoms in the same plane and ideal angles of 120°.

Four election groups give a tetrahedral geometry with the central atom at the center of a tetrahedron and the four electron groups at the corners. The ideal angles between the central atom and any two electron groups is 109.5°.

Five electron groups give a trigonal bipyramidal geometry. A trigonal bipyramid consists of two trigonal pyramids that share the same base with the central atom in the center of the base. The ideal angles in the triangular base are 120°. The electron groups above and below the triangle have a bond angle of 90° to any atom located in the trigonal plane.

Six electron groups give an octahedral geometry with ideal angles of 90°.

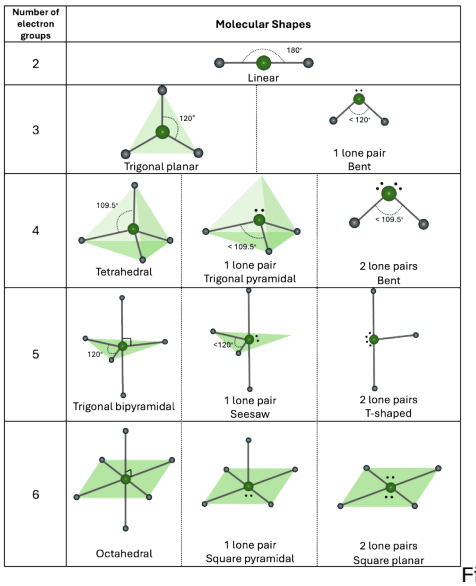
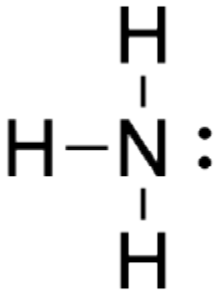


Figure 3.6.3: The basic structures predicted by VSEPR theory to maximize the space around any region of electron density (bonds or lone pairs).

Remember that an electron group can be bonding electrons or lone pairs. How do lone pairs affect the molecular structure? Let's look at the ammonia molecule ($\mathrm{NH_3}$) as an example.



The Lewis structure of $\mathrm{NH_3}$ (left) shows three bonds to hydrogen atoms and one lone pair on nitrogen, making a total of four electron groups. This arrangement gives a tetrahedral electron-pair geometry, with one corner of the tetrahedron occupied by the lone pair (Figure 3.6.4).

However, when we describe the molecular shape, we only consider the positions of the atoms, not the lone pairs. This gives $\mathrm{NH_3}$ a trigonal pyramidal shape (Figure 3.6.4). The ideal bond angle for a tetrahedral shape is 109.5°, but in $\mathrm{NH_3}$, the actual bond angles are slightly smaller. This is because the repulsion between the lone pair and bonding pair electrons is greater than between bonding pair-bonding pair electrons. Bonding electrons are attracted to two nuclei, so they tend to stay between the two nuclei. In contrast, lone pair electrons are only attracted to a single nucleus and spread out more. As a result, the lone pair electrons push the bonding electrons closer together, reducing the bond angle slightly as shown in Figure 3.6.4.

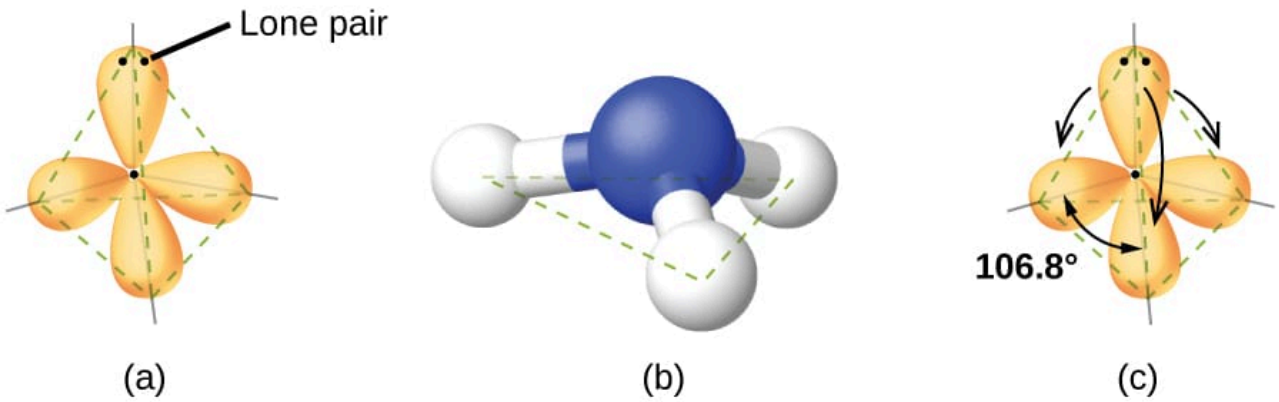


Figure 3.6.4: (a) The four electron groups in NH_3 give a tetrahedral shape with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure results from the lone pair occupying one corner of the tetrahedron. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair repels the bonding electrons more strongly than the bonding electrons repel each other, causing the HNH angle to be smaller than the ideal angle of 109.5°.

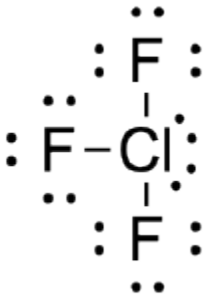
Figure 3.6.3 shows the electron group shapes with the ideal angles as well as the molecular structures that result from lone pairs around the central atom. As discussed in the NH_3 example, lone pair electrons are more repulsive than bonding pair electrons. For this reason, lone pairs tend to occupy sites away from the other atoms. For linear, trigonal planar, and tetrahedral shapes, lone pairs can replace any electron group without changing the molecular structure.

However, in trigonal bipyramidal molecules, there are two different positions:

- Axial positions (surrounded by 90° bond angles)
- Equatorial positions (surrounded by 120° bond angles)

Lone pairs prefer equatorial positions because they have larger bond angles (120°), reducing electron repulsions.

To see how lone pairs influence geometry in a trigonal bipyramidal structure, let's look at chlorine trifluoride (ClF_3).



The Lewis structure of ClF_3 (left) shows three bonds and two lone pairs around the central Cl atom, making a total of five electron groups. This gives a trigonal bipyramidal electron-pair geometry.

However, there are three possible ways to arrange the three bonds and two lone pairs in ClF_3 (Figure 3.6.5). The observed structure has lone pairs in the equatorial positions, resulting in a T-shaped molecular geometry. In a trigonal bipyramidal shape, axial lone pairs would be 90° from three bonds, creating stronger repulsions. In the equatorial position, each lone pair is 90° from only two bonds, which is less repulsive, giving rise to the T-shaped structure, as shown in Figure Figure 3.6.5.

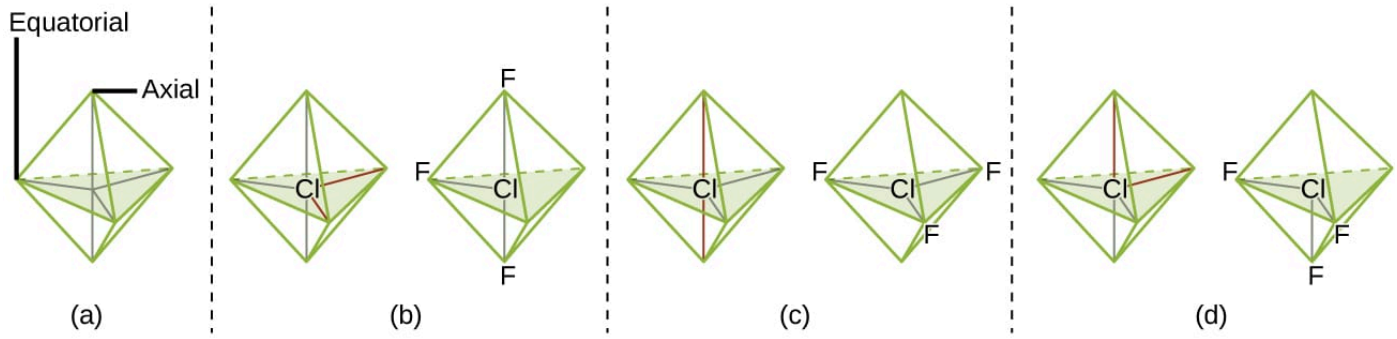


Figure 3.6.5: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in $\mathrm{ClF_3}$ have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the lone pairs both occupying equatorial positions.

Predicting Electron Pair Geometry and Molecular Structure

We can use VSEPR theory to predict molecular shapes using the following steps:

1. Draw the Lewis structure of the molecule or ion, making sure to include lone pairs.
2. Count the number of electron groups (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one electron group.
3. Find the geometry based on the number of electron groups: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 3.6.3.
4. Determine the molecular structure based on the position of the atoms (not lone pairs). If more than one arrangement of lone pairs and 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.

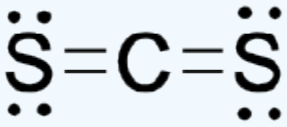
Example 3.6.1: Predicting Molecular Structure: CS_2 and BCl_3

Predict the molecular structure for each of the following:

a. carbon disulfide, $\mathrm{CS_2}$, a colourless liquid.boron trichloride, $\mathrm{BCl_3}$, an important industrial chemical

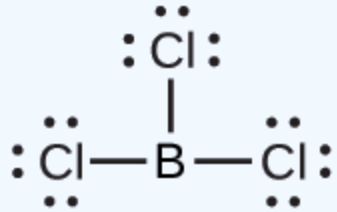
Solution

(a) We write the Lewis structure of $\mathrm{CS_2}$ as:

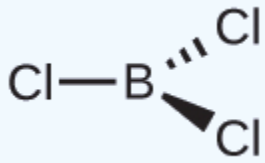


This shows us two regions of high electron density around the carbon atom. Each double bond counts as one electron group and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two electron groups arrange themselves on opposite sides of the central atom with a bond angle of 180°. $\mathrm{CS_2}$ molecules are linear.

(b) We write the Lewis structure of $\mathrm{BCl_3}$ as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar geometry. The $B-Cl$ bonds lie in a plane with 120° angles between them.



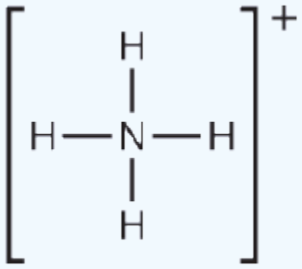
Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Example 3.6.2: Predicting Molecular Structure: Ammonium

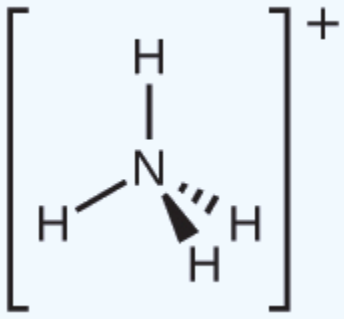
Ammonium nitrate and ammonium sulfate are both used as fertilizers. Predict the structure of the NH_4^+ cation.

Solution

We can write the Lewis structure as:



NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. Four electron groups arrange in a tetrahedral geometry with the central nitrogen atom in the middle:



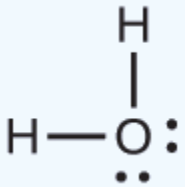
The ammonium ion has a tetrahedral structure.

Example 3.6.3: Predicting Molecular Structure: Lone Pairs on the Central Atom

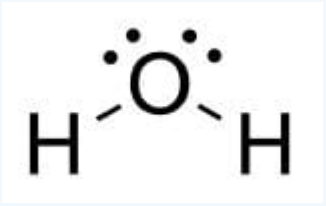
Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of $\mathrm{H_2O}$ indicates that there are four electron groups around the oxygen atom: two lone pairs and two bonds:



There are four groups are arranged in a tetrahedral fashion with two sites occupied by lone pairs.


bent

The ideal $\mathrm{H{-}O{-}H}$ is 109.5°. Experimentally, the bond angle has been found to be 104.5°, which can be attributed to the lone pairs repelling the bonding pair electrons more strongly than the bonding pairs repel each other. For CHM 135H, knowing the ideal angles is sufficient.

Exercise 3.6.1

The hydronium ion, $\mathrm{H_3O^+}$, forms when acids are dissolved in water. What is the structure of $\mathrm{H_3O^+}$?

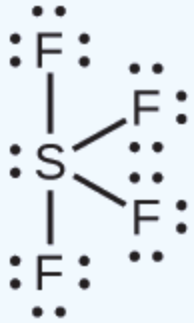
Answer available at the end of this section.

Example 3.6.4: Predicting Molecular Structure: SF_4

Sulfur tetrafluoride, $\mathrm{SF_4}$, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides . What is the structure of $\mathrm{SF_4}$?

Solution

The Lewis structure of $\mathrm{SF_4}$ indicates five electron groups around the sulfur atom: one lone pair and four bonding pairs:



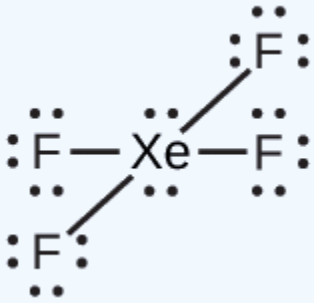
We expect these five electron groups to adopt a trigonal bipyramidal geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions, giving a seesaw structure.

Example 3.6.5: Predicting Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the structure of the $\mathrm{XeF_4}$ molecule.

Solution

The Lewis structure of $\mathrm{XeF_4}$ indicates six electron groups around the xenon atom: two lone pairs and four bonds:



These six electron groups adopt an octahedral arrangement. To minimize repulsions, the lone pairs should be on opposite sides of the central atom The five atoms are all in the same plane and have a square planar molecular structure.

Molecular Polarity and Dipole Moment

As discussed earlier, polar covalent bonds form when two atoms have different electronegativities. This causes one atom to have a partial positive charge (δ⊕) and the other to have a partial negative charge (δ⊖) as electrons are pulled toward the more electronegative atom. This separation of charge creates a bond dipole moment, which depends on both the electronegativity difference between atoms and the bond length.

A molecule as a whole may also have a dipole moment, depending on its molecular structure and the polarity of its bonds. If a molecule has an overall separation of charge, it is polar. If its bond dipoles cancel each other out, the molecule is nonpolar. The dipole moment of a molecule is determined by adding up the bond dipole moments in three-dimensional space.

For diatomic molecules, molecular polarity is determined by the single bond in the molecule. Homonuclear diatomic molecules such as $\mathrm{Br_2}$ and $\mathrm{N_2}$ have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

For molecules with more than one bond, the molecular geometry must be considered. In CO_2, the $C{=}O$ bonds are polar, but the molecule is linear. Since the bond dipoles point in opposite directions, they cancel, and the molecule is nonpolar (Figure $3.6.6$). In contrast, the water molecule (H_2O) also has two polar bonds, but its bent molecular structure prevents the bond dipoles from cancelling. As a result, H_2O has a net dipole moment and is polar.

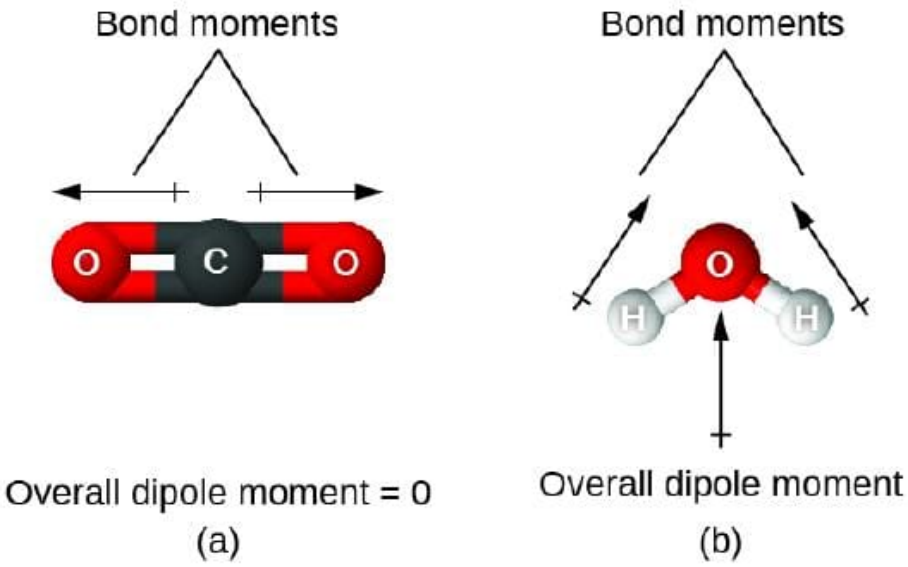


Figure $3.6.6$: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

To summarize, for a molecule to be polar, it must meet two conditions:

1. It must contain at least one polar covalent bond.
2. Its molecular structure must be asymmetrical, so the bond dipoles do not cancel out

Example $3.6.6$

Which of the following molecules has a dipole moment?

a) NH_3

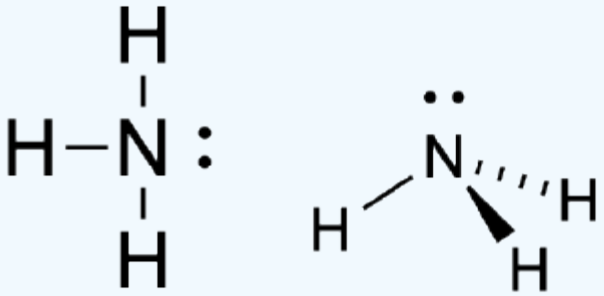
b) CF_4

c) SO_2

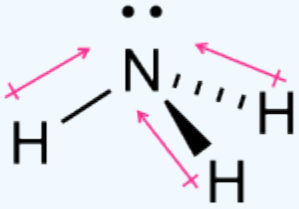
Solution

We need to know the shape of the molecule, so we need to start with the Lewis structure

a) From the Lewis structure (3 bonds + 1 lone pair) we know NH_3 is trigonal pyramidal

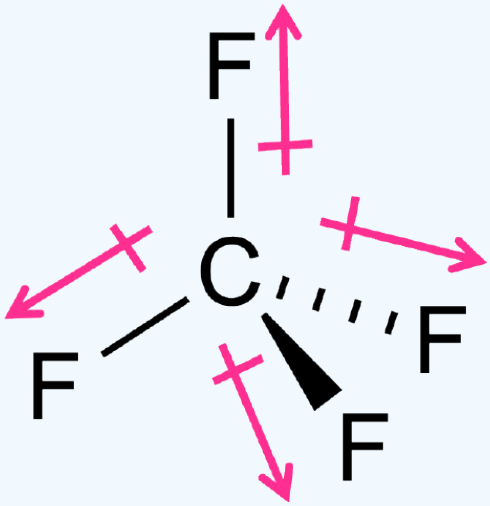


N is more electronegative than H, so the bond dipoles are pointed towards N.

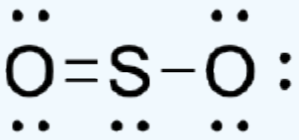


The bond dipoles do not cancel, so $\mathrm{NH_3}$ has a dipole moment.

b) $\mathrm{CF_4}$ is a tetrahedral molecule. The $\mathrm{C-F}$ bonds are polar, but the bond dipoles cancel, so there is no dipole moment for the molecule.

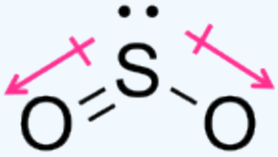


c) First consider the Lewis structure of $\mathrm{CO_2}$:



The central atom, S, has a lone pair and two bonds, so 3 electron groups. This gives a trigonal planar geometry with a lone pair occupying one site, leading to a bent molecule.

The $\mathrm{S-O}$ bonds are polar with O having a greater electronegativity than S.



The bond dipoles do not cancel, so SO_2 has a dipole moment.

Properties of Polar Molecules

Polar molecules behave differently from nonpolar molecules in certain situations. For example, when placed in an electric field, polar molecules align themselves with the positive end facing the negative plate and the negative end facing the positive plate (Figure 3.6.7). An electrically charged object can attract polar molecules but has no effect on nonpolar ones. This difference in polarity also explains solubility trends. Polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

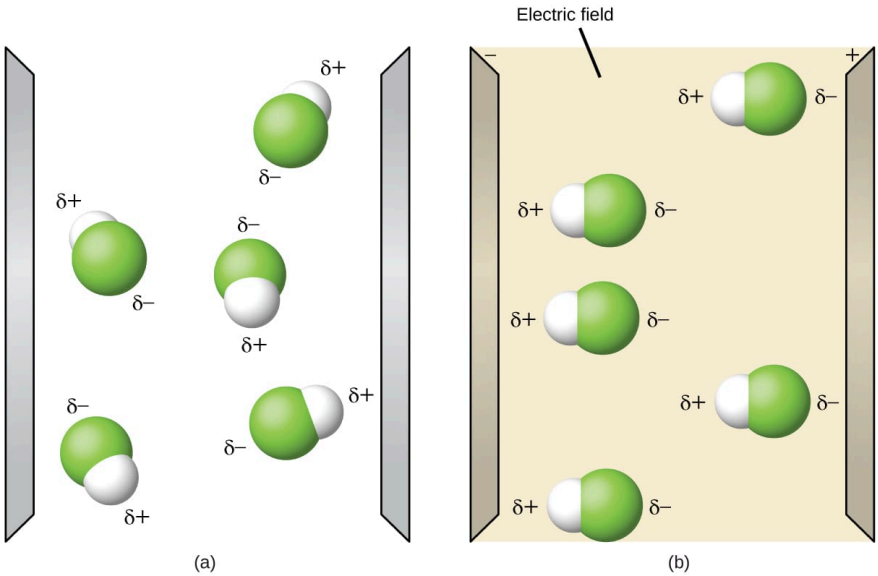


Figure 3.6.7: (a) Molecules are randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. This model is based on minimizing repulsions between electron groups (bonds and lone pairs) by maximizing their distance from each other.

The basic molecular shapes predicted by VSEPR are:

- No lone pairs on the central atom: Linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral.
- With lone pairs: Bent, trigonal pyramidal, seesaw, T-shaped, square planar, and square pyramidal.

Lone pairs tend to occupy positions that minimize repulsions with other electron groups.

A dipole moment measures charge separation in a molecule. For a single bond, the bond dipole moment is determined by electronegativity differences between atoms. For a molecule as a whole, the dipole moment depends on both individual bond moments and their arrangement in space. Polar molecules interact with electric fields, while nonpolar molecules do not.

Glossary

axial position
: The location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle.

bond angle
: The the angle between two bonds that share an atom, measured in degrees.

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

equatorial position
: One of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle.

linear geometry
: 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 geometry
: 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
: A molecule with an overall dipole moment.

tetrahedral geometry
: Shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom.

trigonal bipyramidal geometry
: Shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane.

trigonal planar geometry
: Shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom.

Answers

Exercise 3.6.1

trigonal pyramidal

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3.7: Intermolecular Forces

Learning Objectives

- Describe the types and relative strengths of intermolecular forces possible between atoms or molecules (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Relate the strength of the intermolecular forces to physical properties, such as boiling point.

So far, we have focused on the forces within molecules, or intramolecular forces, which include covalent and ionic bonds. In this section, we will explore intermolecular forces (IMFs)—the forces of attraction between molecules. While IMFs are also electrostatic in nature, they are much weaker than chemical bonds but play a critical role in determining the physical properties of substances.

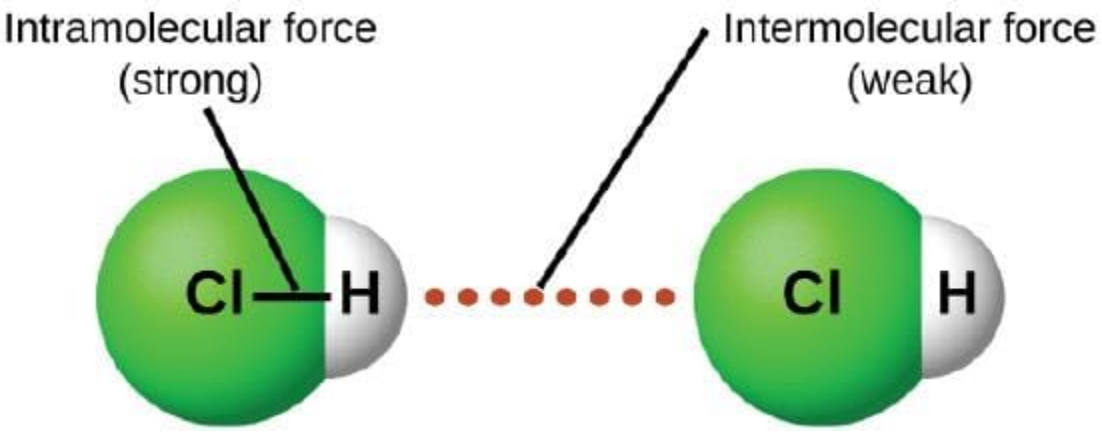


Figure 3.7.1: Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and influence boiling points, melting points, and solubility.

Intermolecular forces and the State of Matter

Intermolecular forces strongly influence a substance's physical state. Consider the three states of matter:

- In solids, particles are closely packed and vibrate in place.
- In liquids, particles are still close together but can move past each other.
- In gases, particles are far apart and move freely.

The phase of a substance depends on the balance between intermolecular forces and kinetic energy (KE). IMFs hold molecules together, while kinetic energy provides the energy required to overcome the attractive forces and thus increase the distance between molecules. The kinetic energy of a system is defined by its temperature and Figure 3.7.2 illustrates how increasing temperature and therefore increasing kinetic energy can cause phase changes.

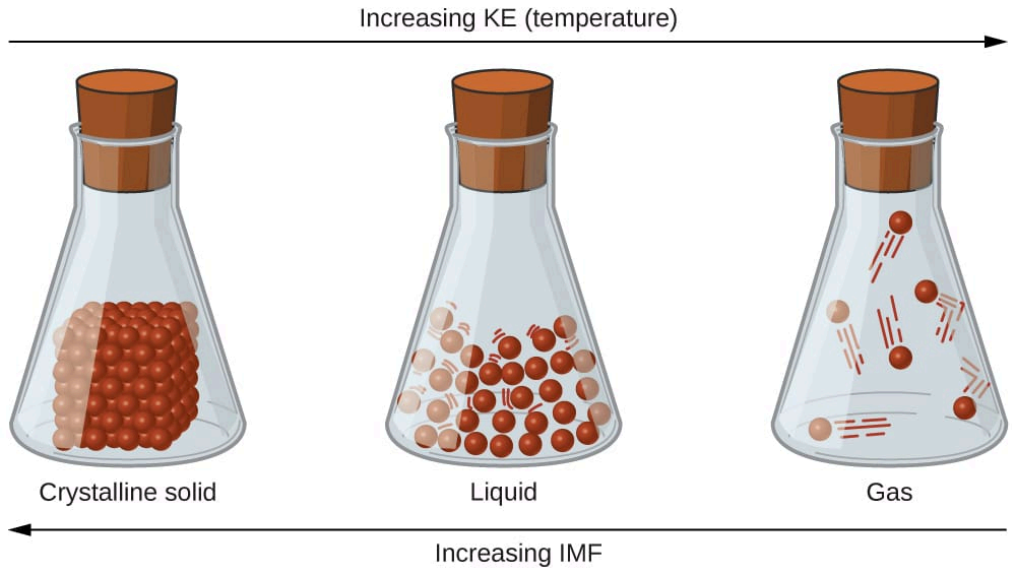


Figure 3.7.2: Transitions between solid, liquid, and gaseous states of a substance occur when temperature favors the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

To illustrate the processes shown in this figure, consider water vapor. When gaseous water is cooled sufficiently, the attractions between $\mathrm{H_2O}$ molecules can hold the molecules together when they come into contact with each other. This causes the water vapor to condense, forming liquid $\mathrm{H_2O}$. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure 3.7.3.



Figure 3.7.3: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, so that the attractions between the molecules are strong relative to their kinetic energy. Consequently, they form liquids. Butane, $\mathrm{C_4H_{10}}$, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state (Figure 3.7.4).



Figure 3.7.4: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by “Sam-Cat”/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough kinetic energy to overcome the intermolecular forces between them and move past each other, and a solid forms.

There are different types of intermolecular forces between molecules, including dispersion forces, dipole-dipole interactions, and hydrogen bonding. Ion-dipole forces also exist between molecules and ions. The strengths of these attractive forces vary widely, although the intermolecular forces between small molecules are usually weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the intermolecular forces in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules (Figure 3.7.1.

Dispersion Forces

All atoms and molecules experience dispersion forces, which arise due to temporary shifts in electron distribution. Because electrons are constantly moving, an atom or molecule can develop a temporary dipole when its electrons become unevenly distributed. This dipole can then induce a dipole in a nearby atom or molecule, leading to a weak attraction between them (Figure 3.7.5).

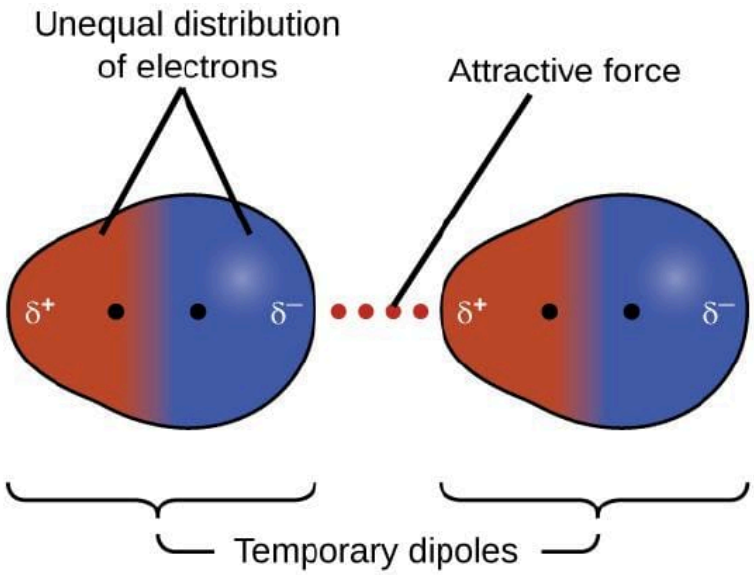


Figure 3.7.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces increase with atomic and molecular size. For example, among the halogens, F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Melting and boiling points increase as atomic size and dispersion forces increase., as seen in Table 3.7.1.

Table 3.7.1: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

Why do larger atoms Have stronger dispersion forces? Larger atoms have more electrons, and their valence electrons are farther from the nucleus. Because they are less tightly held, their electron clouds are easier to distort, meaning they can form temporary dipoles more easily.

The ease with which a molecule's electron cloud is distorted is called polarizability.

- Highly polarizable molecules have strong dispersion forces because their electron clouds can shift easily.
- Less polarizable molecules have weaker dispersion forces because their electron clouds are more rigid.

Example 3.7.1: London Forces and Their Effects

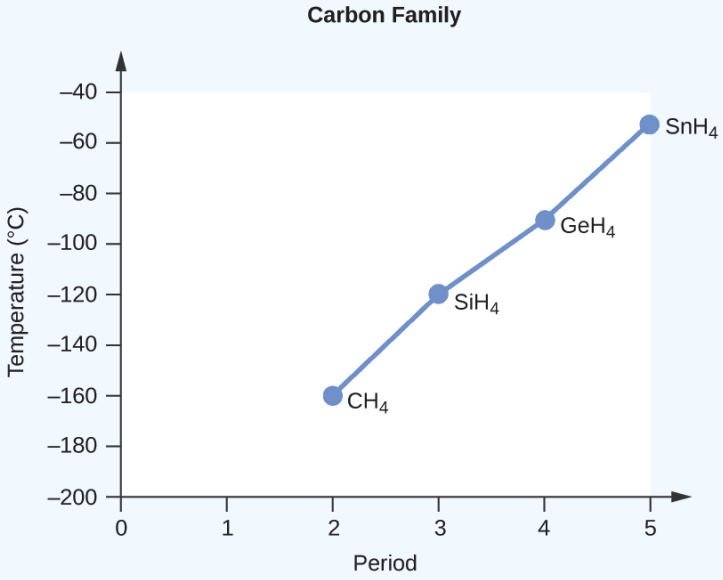
Order the following compounds from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

C, Si, Ge, and Sn are in the same column of the periodic table and thus have the same number of valence electrons. All four compounds have a tetrahedral geometry and are therefore nonpolar. The only intermolecular forces between the molecules are dispersion forces. Smaller molecules are less polarizable and have weaker dispersion forces. Weaker attractions between molecules require less kinetic energy to overcome the intermolecular forces and therefore the boiling point is lower. The

molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 < SiH_4 < GeH_4 < SnH_4$.

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:



Exercise 3.7.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer available at the end of this section.

The shape of a molecule affects the strength of its dispersion forces by influencing how much surface area is available for molecular interactions. Molecules with larger surface areas experience stronger dispersion forces because they have more contact points with neighbouring molecules.

For example, boiling points for *n*-pentane, isopentane, and neopentane (shown in Figure 3.7.6) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though all three molecules have the same chemical formula, their boiling points are different because their shapes affect the strength of dispersion forces. n-Pentane is elongated, providing more surface area for intermolecular contact. This allows for stronger dispersion forces and a higher boiling point. Isopentane has a more compact shape, reducing the available surface area for interactions, leading to weaker dispersion forces and a lower boiling point. Neopentane is the most compact, offering the least surface area for molecular interactions. As a result, it has the weakest dispersion forces and the lowest boiling point.

This behavior is similar to VELCRO brand fasteners. A long strip of Velcro creates stronger connections because it has more surface area in contact. A small patch of Velcro forms weaker connections because less of it is available for attachment. Likewise, larger molecules with greater surface contact experience stronger dispersion forces, just as longer Velcro strips create stronger connections.

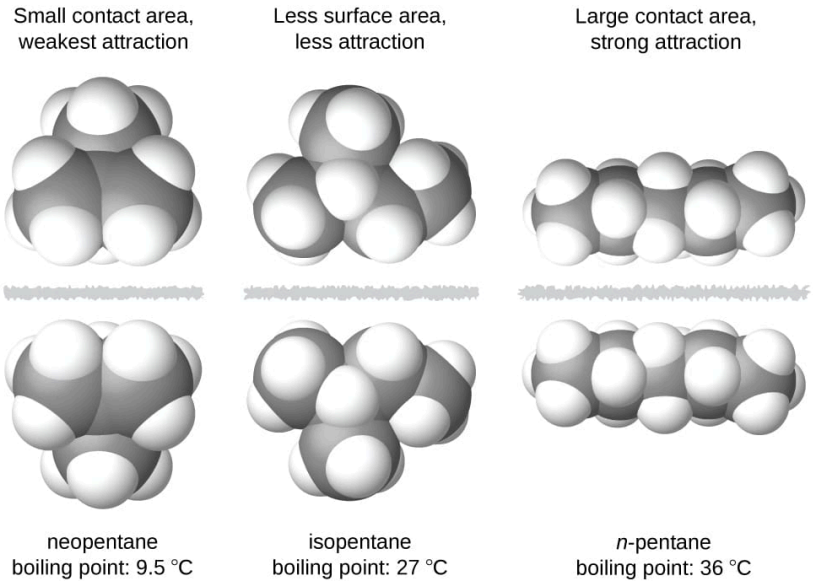


Figure 3.7.6: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Chemistry in Everyday Life: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 3.7.7, with a large surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally non-sticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Later research led by Alyssa Stark at University of Akron showed that geckos can maintain their hold on hydrophobic surfaces (similar to the leaves in their habitats) equally well whether the surfaces were wet or dry. Stark's experiment used a ribbon to gently pull the geckos until they slipped, so that the researchers could determine the geckos' ability to hold various surfaces under wet and dry conditions. Further investigations may eventually lead to the development of better adhesives and other applications.

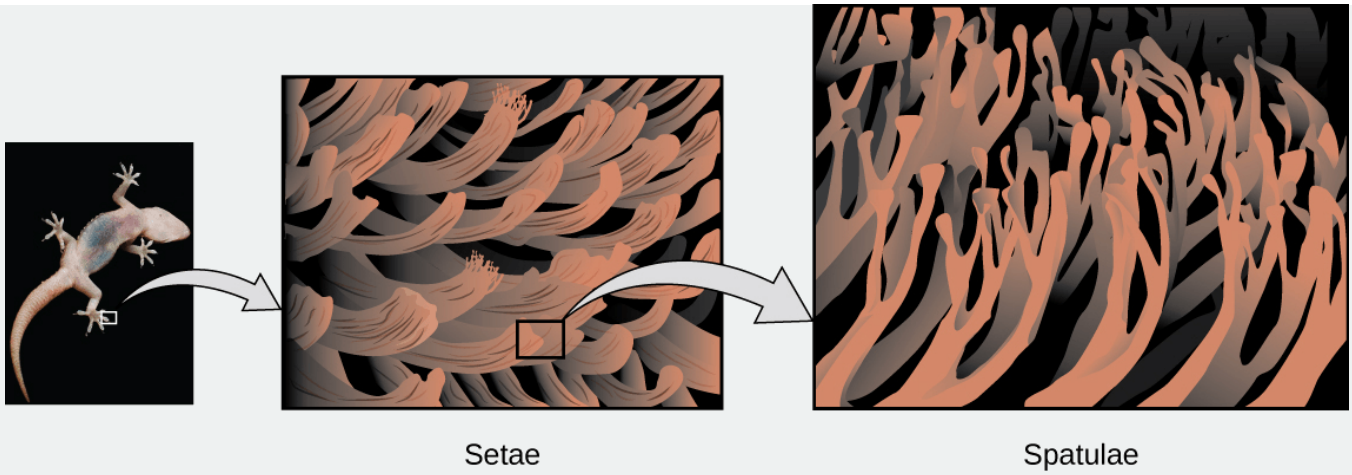


Figure 3.7.7: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)Dipole-Dipole Attractions

Dipole-Dipole Forces

As discussed in Section 3.6, polar molecules have a separation of charge due to differences in electronegativity. This results in a partially positive end (δ⁺) and a partially negative end (δ⁻), forming a dipole.

Because opposite charges attract, polar molecules experience dipole-dipole attractions—the electrostatic force between the δ⁺ end of one molecule and the δ⁻ end of another. A good example is hydrogen chloride (HCl). In HCl, chlorine (Cl) is more electronegative, so it carries the partial negative charge (δ⁻), while hydrogen (H) carries the partial positive charge (δ⁺). The attraction between opposite dipoles of neighboring HCl molecules creates dipole-dipole forces (Figure 3.7.8).

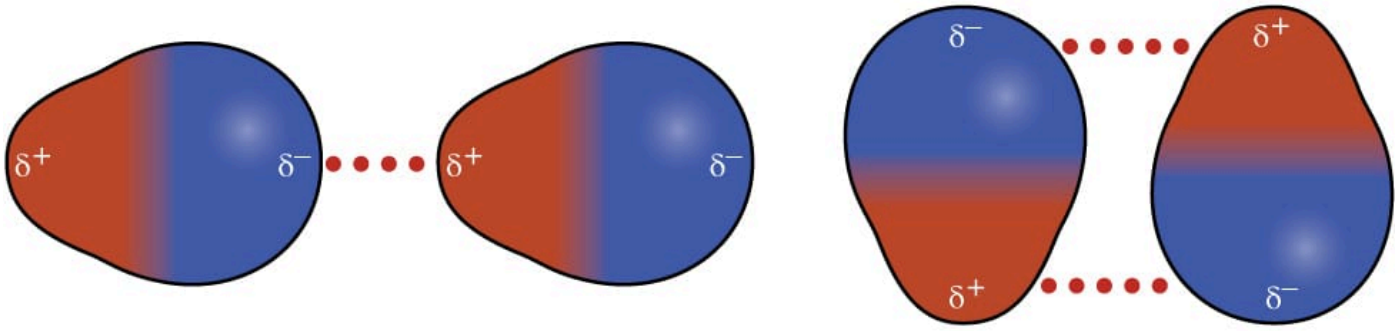


Figure 3.7.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of dipole-dipole forces can be seen when comparing the properties of HCl (polar) and F_2 (nonpolar). Both HCl and F_2 have similar molecular masses. At 150 K, the molecules of both substances have the same average kinetic energy. However, HCl remains a liquid, while F_2 stays a gas.

Why? The dipole-dipole attractions in HCl are strong enough to keep molecules close together, preventing them from escaping into the gas phase. In contrast, F_2 molecules only experience weak dispersion forces, which are not strong enough to hold them together as a liquid at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is also a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules.

Since stronger intermolecular forces require more energy to overcome, boiling and freezing points are useful indicators of IMF strength.

Example 3.7.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar dispersion forces. Because CO is a polar molecule, it also experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Exercise 3.7.2

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer available at the end of this section.

Hydrogen Bonding

Hydrogen bonding is a particularly strong type of dipole-dipole attraction that occurs when a hydrogen atom is covalently bonded to fluorine (F), oxygen (O), or nitrogen (N)—the three most electronegative elements.

This leads to a large electronegativity difference, creating a strong partial positive charge (δ⊕) on hydrogen and a strong partial negative charge (δ⊖) on the electronegative atom. Additionally, because hydrogen, fluorine, oxygen, and nitrogen are all small atoms, the charged regions can get very close together, further strengthening the electrostatic attraction between molecules. Figure 3.7.9 illustrates hydrogen bonding with the dotted lines between water molecules.

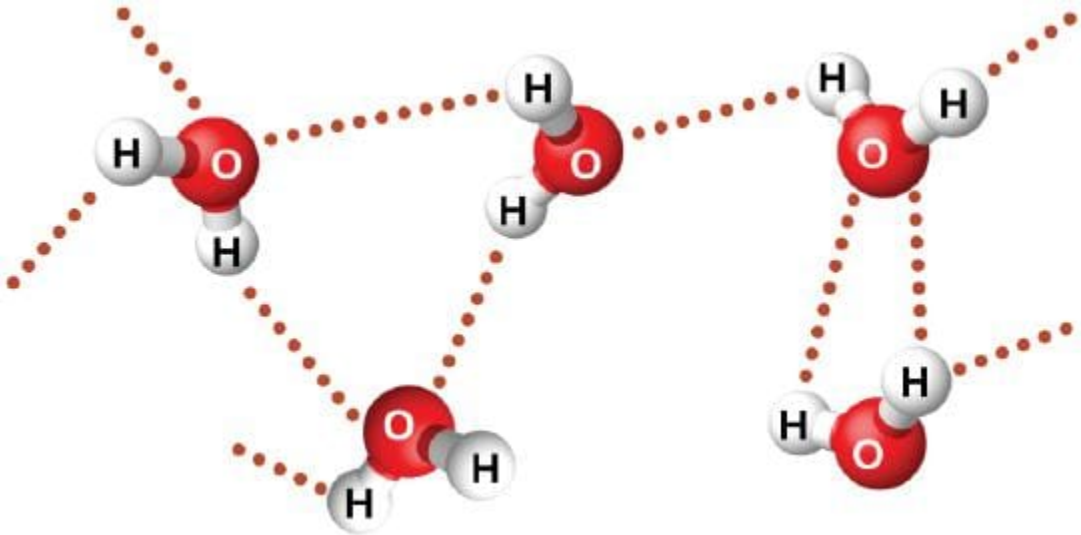


Figure 3.7.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite the name "hydrogen bond," these interactions are not actual chemical bonds. They are intermolecular forces—weaker than covalent bonds (only 5–10% as strong) but stronger than regular dipole-dipole attractions and much stronger than dispersion forces.

Hydrogen bonds significantly affect the properties of liquids and solids. For example, consider the boiling points of binary hydrides in groups 15 (NH_3, PH_3, AsH_3, SbH_3), 16 (H_2O, H_2S, H_2Se, H_2Te), and 17 (HF, HCl, HBr, HI). Figure 3.7.10 shows the boiling points of the heaviest three hydrides in each group. As we move down these groups, the molecule polarities decrease slightly and the molecular sizes increase substantially. Stronger dispersion forces outweigh weaker dipole-dipole attractions, causing boiling

points to rise steadily.

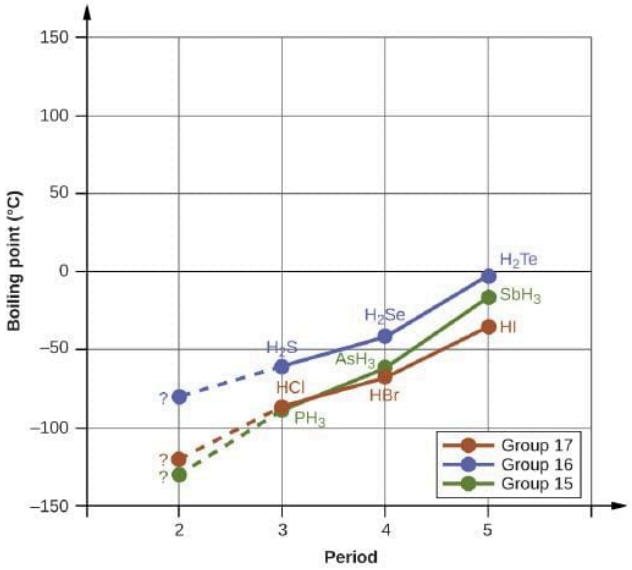


Figure 3.7.10: For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 3.7.11. The stark contrast between those predictions and reality provides compelling evidence for the strength of hydrogen bonding.

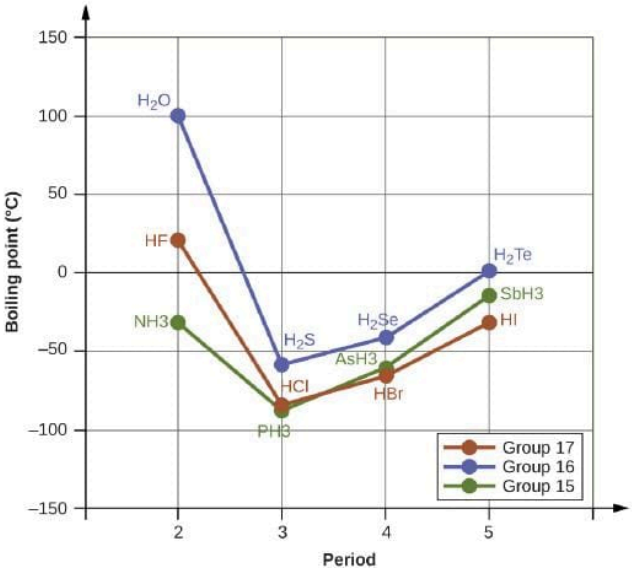


Figure 3.7.11: In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

Example 3.7.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an $-OH$ group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3$ < CH_3OCH_3 < CH_3CH_2OH. The boiling point of propane is –42.1 °C, the boiling point of dimethylether is –24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 3.7.3

Ethane (CH_3CH_3) has a melting point of –183 °C and a boiling point of –89 °C. Would you expect the melting and boiling points of methylamine (CH_3NH_2) to be higher or lower than for ethane? Explain your reasoning.

Answer available at the end of this section.

How Sciences Interconnect: Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 3.7.12.

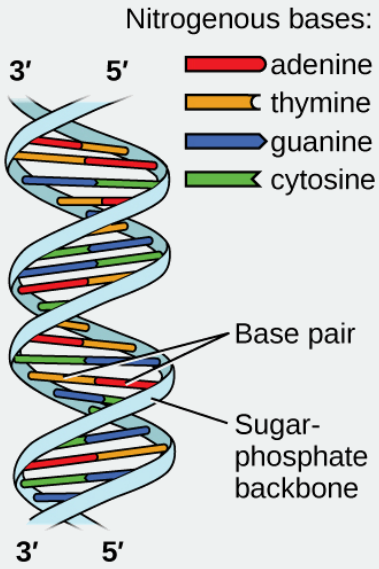


Figure 3.7.12: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 3.7.13.

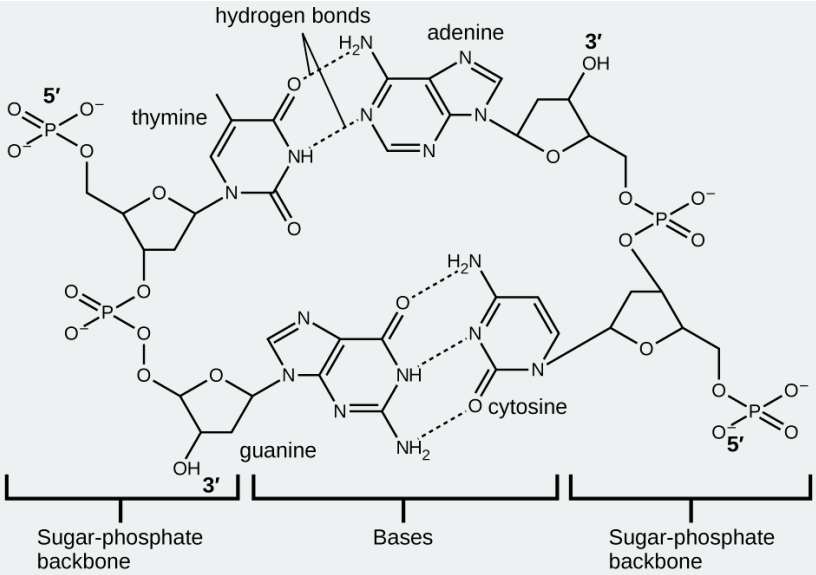


Figure 3.7.13: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Intermolecular Forces Involving Ions

So far, we’ve focused on intermolecular forces between neutral molecules (or atoms), and how the strength of these interactions depends on factors such as size, shape, polarity, and polarizability. But how do ions fit into this discussion?

All intermolecular forces arise from electrostatic attractions between regions of positive and negative charge. The strength of these forces depends on the size and permanence of those charges. Ions, which carry full, permanent charges, interact more strongly than any neutral molecule can. As a result, ion–ion interactions (also known as ionic bonds) are much stronger than any intermolecular force between neutral particles.

These strong interactions are responsible for the structure and stability of ionic solids like sodium chloride. Unlike a covalent bond, which is directional and involves shared electrons between two atoms, an ionic bond is a nondirectional attraction between oppositely charged ions. The ions arrange themselves so that each cation is surrounded by anions and vice versa, forming a highly stable lattice held together by electrostatic forces.

Although ion–ion interactions in ionic solids are very strong, ions can also interact with polar molecules, which have partial charges. For example, when a salt dissolves in water, water molecules surround each ion and form ion–dipole interactions. These are weaker than the original ion–ion attractions in the solid, but many ion–dipole interactions form for each ion pair. This can compensate for the energy required to separate the ions and allow the salt to dissolve.

Because the same physical principle (opposite charges attract) underlie both ionic bonding and intermolecular forces, you can think of ionic bonding as a very strong form of electrostatic interaction, in some ways like an extremely strong intermolecular force between full permanent charges. Depending on the context, it can be helpful to think of ionic bonding either as a chemical bond (when describing salt structures) or as a strong intermolecular force (when considering solubility and ion–dipole interactions). Whether we call it an ionic bond or an ion–ion interaction, the important thing is recognizing that both describe the same physical force, the attraction between full, opposite charges. This attraction explains why ionic solids are stable, why salts dissolve in polar solvents, and why ions interact so strongly with other charged or partially charged species.

Summary

Intermolecular forces (IMFs) are electrostatic forces of attraction between molecules that influence physical properties such as boiling points, melting points, and phase changes.

There are three main types of intermolecular forces:

- Dipole-dipole forces occur between polar molecules, where the partially negative end of one molecule is attracted to the partially positive end of another.
- Hydrogen bonds are a particularly strong type of dipole-dipole force that occurs when hydrogen is bonded to fluorine (F), oxygen (O), or nitrogen (N)—the three most electronegative elements.
- Dispersion forces (also called London forces) arise from temporary shifts in electron distribution that create momentary dipoles, inducing weak attractions between molecules. These forces increase in strength as molecular size and electron cloud polarizability increase.

Glossary

dipole-dipole attraction
: Intermolecular attraction between two permanent dipoles.

dispersion force
: Attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together; also called London dispersion force.

hydrogen bonding
: Occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

induced dipole
: A temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule.

intermolecular force
: Noncovalent attractive force between atoms, molecules, and/or ions.

ion-dipole attraction
: Electrostatic attraction between an ion and a polar molecule.

Answers

Exercise $3.7.1$

$\mathrm{C_2H_6} < \mathrm{C_3H_8} < \mathrm{C_4H_{10}}$. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore $\mathrm{C_2H_6} < \mathrm{C_3H_8} < \mathrm{C_4H_{10}}$.

Exercise $3.7.2$

ICl. ICl and $\mathrm{Br_2}$ have similar masses (~160 amu) and therefore experience similar dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; $\mathrm{Br_2}$ is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Exercise $3.7.3$

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. $\mathrm{CH_3CH_3}$ and $\mathrm{CH_3NH_2}$ are similar in size and mass, but methylamine possesses an $-\mathrm{NH}$ group and can have hydrogen bonding between molecules . This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

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3.E: Bonding and Intermolecular Forces (Exercises)

Chemical Bonding

Exercise $3.E.1$*

What information can you use to predict whether a bond between two atoms is covalent or ionic?

Answer available at the end of this section.

Exercise $3.E.2$*

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

1. $\mathrm{Cl_2CO}$
2. MnO
3. $\mathrm{NCl_3}$
4. $\mathrm{CoBr_2}$
5. $\mathrm{K_2S}$
6. CO

Answer available at the end of this section.

Ionic Bonding

Exercise $3.E.3$**

Why is it incorrect to speak of a **molecule** of solid NaCl?

Answer available at the end of this section.

Exercise $3.E.4$*

How does an atom form a cation, a positively charged ion?

Answer available at the end of this section.

Exercise $3.E.5$*

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

P, Mg, Al, O, Cl, Cs

Answer available at the end of this section.

Exercise $3.E.6$*

Write the electron configuration for each of the following ions:

As^{3-}, I^{-}, Be^{2+}, O^{2-}, Al^{3+}

Answer available at the end of this section.

Exercise $3.E.7$**

Predict the formula of the binary compounds made of the following elements.

(a) Mg and S

(b) K and O

(c) Ga and Cl

(d) Li and N

Answer available at the end of this section.

Covalent Bonding

Exercise $3.E.8$*

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond. Which best describes the $O-H$ bond in water?

Answer available at the end of this section.

Exercise $3.E.9$*

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) P or S

(d) Si or N

(e) Ba or P

Answer available at the end of this section.

Exercise $3.E.10$*

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, N, O

(b) Br, Cl, F, I

(c) F, O, P, S

(d) Al, Na, O, P

Answer available at the end of this section.

Exercise 3.E.11**

Which is the most polar bond?

C–C, C–H, N–H, O–H, Se–H

Answer available at the end of this section.

Lewis Structures

Exercise 3.E.12*

Draw the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

Answer available at the end of this section.

Exercise 3.E.13**

Draw Lewis structures for the following:

a) AsF_3

b) $SiCl_4$

c) H_2CO

d) H_3O^+

e) BF_4^-

f) ClNO

g) NH_4^+

h) HCCH

i) ClCN

Answer available at the end of this section.

Exercise $3.E.14$*

How are single, double, and triple bonds similar? How do they differ?

Answer available at the end of this section.

Molecular Structure and Polarity

Exercise $3.E.15$*

For each of the Lewis structures in Exercise 13, predict the geometry of the molecule or ion and the ideal angles about the central atom.

a) $\mathrm{AsF_3}$

b) $\mathrm{SiCl_4}$

c) $\mathrm{H_2CO}$

d) $\mathrm{H_3O^+}$

e) $\mathrm{BF_4^-}$

f) ClNO

g) $\mathrm{NH_4^+}$

h) HCCH

i) ClCN

Answer available at the end of this section.

Exercise $3.E.16$**

Predict the geometry of each of the following molecules:

a) $\mathrm{SF_6}$

b) $\mathrm{PCl_5}$

c) $\mathrm{ICl_3}$

Answer available at the end of this section.

Exercise $3.E.17$*

Explain how a molecule that contains polar bonds can be nonpolar.

Answer available at the end of this section.

Exercise $3.E.18$***

Which of the following molecules contain polar bonds? Which of these molecules have dipole moments?

a) $\mathrm{SF_6}$

b) $\mathrm{ICl_3}$

c) $\mathrm{BF_3}$

d) $\mathrm{SeF_4}$

Answer available at the end of this section.

Exercise $3.E.19$***

Which of the following molecules have dipole moments?

a) $\mathrm{CCl_2F_2}$

b) $\mathrm{CF_4}$

c) $\mathrm{PCl_3}$

d) ClNO (N is the central atom)

Answer available at the end of this section.

Intermolecular Forces

Exercise $3.E.20$*

Describe the following intermolecular forces:

dispersion force

dipole-dipole attraction

hydrogen bond

Answer available at the end of this section.

Exercise $3.E.21$***

Identify the intermolecular forces present in the following molecules:

$\mathrm{CH_3CH_2OH}$, $\mathrm{CH_3CH_2CH_3}$, $\mathrm{CH_3CH_2Cl}$

Of the intermolecular forces present, which is the strongest for each molecule?

Answer available at the end of this section.

Exercise $3.E.22$***

Carbon tetrachloride, CCl_4, was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. What intermolecular forces are present between molecules of carbon tetrachloride? Between molecules of phosgene?

Answer available at the end of this section.

Exercise $3.E.23$**

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

Answer available at the end of this section.

Exercise $3.E.24$**

Neon and HF have approximately the same molecular masses. Why do the boiling points of Ne and HF differ?

Answer available at the end of this section.

Exercise $3.E.25$***

Arrange each of the following sets of compounds in order of increasing boiling temperature:

a) HCl, H_2O, SiH_4

b) F_2, Cl_2, Br_2

Answer available at the end of this section.

Exercise $3.E.26$**

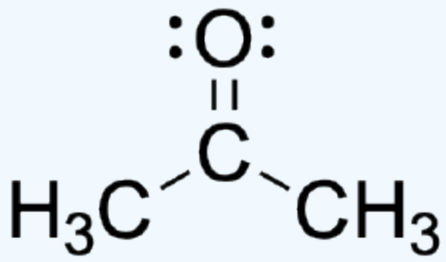
The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer.

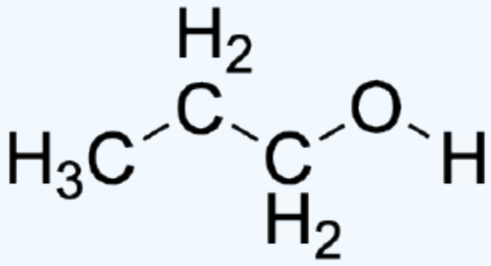
Answer available at the end of this section.

Additional Problems

Exercise $3.E.27$**

Based on intermolecular forces, explain the differences in the boiling points of acetone (56.2 °C) and propan-1-ol (97.4 °C), which have similar molar masses.





acetone propan-1-ol

Answer available at the end of this section.

Exercise $3.E.28$**

Identify the atoms that correspond to each of the following electron configurations. What is the common ion formed from each atom?

a) $1s^2 2s^2 2p^5$

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

c) $1s^2 2s^2 2p^6 3s^2 3p^3$

Answer available at the end of this section.

Exercise $3.E.29$***

Which atoms can form a polar covalent bond to sulfur with a partial positive charge on the sulfur atom?

Answer available at the end of this section.

Exercise $3.E.30$**

What is the charge on X in each ionic compound?

(a) $\mathrm{CaX_2}$

(b) $\mathrm{Al_2X_3}$

(c) $\mathrm{X(OH)_2}$

Answer available at the end of this section.

Exercise $3.E.31$***

The molecule $\mathrm{XF_3}$ has a dipole moment. Is X boron or phosphorus?

Answer available at the end of this section.

Exercise $3.E.32$***

a) Why is the $\mathrm{H{-}N{-}H}$ angle in $\mathrm{NH_3}$ smaller than the $\mathrm{H{-}C{-}H}$ bond angle in $\mathrm{CH_4}$?

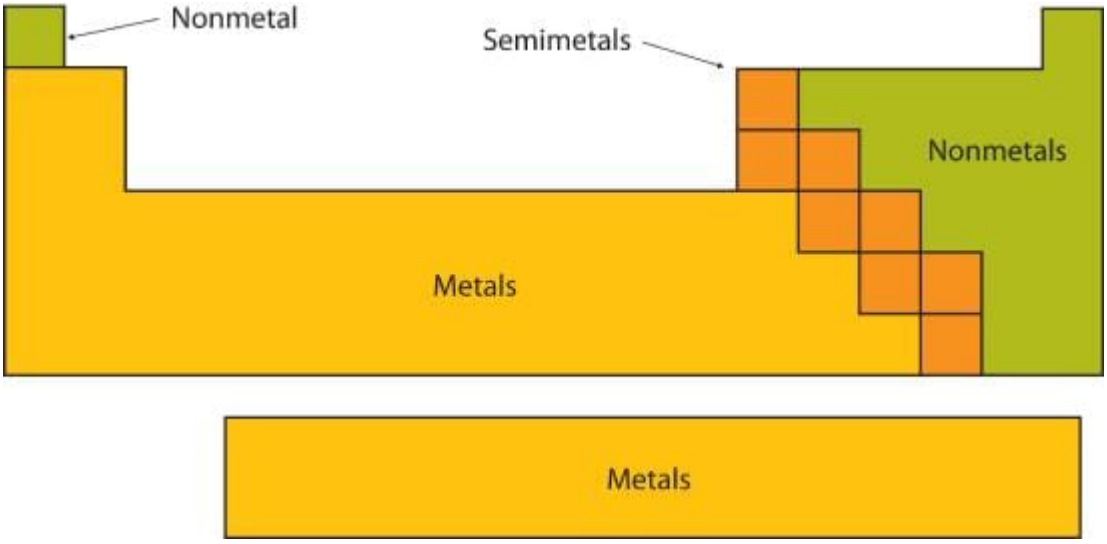
b) Why is the $\mathrm{H{-}N{-}H}$ angle in $\mathrm{NH_4^+}$ identical to the $\mathrm{H{-}C{-}H}$ bond angle in $\mathrm{CH_4}$?

Answer available at the end of this section.

Answers

Exercise $3.E.1$*

Ionic bonds form between a metal and a non-metal. Covalent bonds form between non-metals. The position on the periodic table can be used to determine if an element is a metal or a non-metal.



Exercise $3.E.2$*

ionic: (2), (4), (5); covalent: (1), (3), (6)

Exercise $3.E.3$**

NaCl consists of ions arranged in a three-dimensional lattice, not covalently bonded molecules.

Unlike covalent molecules, which are discrete entities with a specific number of atoms bonded together (like $\mathrm{H_2O}$ or $\mathrm{CO_2}$), an ionic lattice doesn't have a distinct "molecule" unit. Instead, it consists of a continuous network of ions.

Exercise $3.E.4$*

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Cations form when electrons are lost from the neutral atom.

$\mathrm{P^{3-}}$; $\mathrm{Mg^{2+}}$; $\mathrm{Al^{3+}}$; $\mathrm{O^{2-}}$; $\mathrm{Cl^-}$; $\mathrm{Cs^+}$

Exercise $3.E.6$*

$\mathrm{As^{3-}}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ or $[\mathrm{Kr}]$

$\mathrm{I^-}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ or $[\mathrm{Xe}]$

$\mathrm{Be^{2+}}$: $1s^2$ or $[\mathrm{He}]$

$\mathrm{O^{2-}}$: $1s^2 2s^2 2p^6$ or $[\mathrm{Ne}]$

$\mathrm{Al^{3+}}$: $1s^2 2s^2 2p^6$ or $[\mathrm{Ne}]$

Exercise $3.E.7$**

(a) Mg forms $\mathrm{Mg^{2+}}$; S forms $\mathrm{S^{2-}}$: MgS

(b) K forms $\mathrm{K^+}$; O forms $\mathrm{O^{2-}}$: $\mathrm{K_2O}$

(c) Ga forms $\mathrm{Ga^{3+}}$; Cl forms $\mathrm{Cl^-}$: $\mathrm{GaCl_3}$

(d) Li forms $\mathrm{Li^+}$; N forms $\mathrm{N^{3-}}$: $\mathrm{Li_3N}$

Exercise $3.E.8$*

A nonpolar covalent bond is formed between atoms that share the electron pair(s) equally - the bonding atoms have the same or very similar electronegativities. A polar covalent bond is formed between atoms with different electronegativities. The more electronegative atom of the bond attracts the shared electrons more strongly, resulting in a partial negative charge on this atom. The less electronegative atom which attracts the shared electrons less strongly has a partial positive

charge. An ionic bond is formed from atoms with large differences in electronegativities (metals and non-metals) such that the electrons are not shared, but rather transferred from the metal (forming a metal cation) to the non-metal (forming an anion).

The $\mathrm{O{-}H}$ bond is a polar covalent bond in which the electrons are shared, but not equally. O is more electronegative than H so there is a partial negative charge on the O atom and a partial positive charge on the H atom.

Exercise $3.E.9$**

(a) Cl - electronegativity decreases down a column as the atomic radius increases

(b) O - electronegativity increases across a period as the atomic radius decreases

(c) S - electronegativity increases across a period as the atomic radius decreases

(d) N - electronegativity increases across a period as the atomic radius decreases and electronegativity decreases down a column as the atomic radius increases

(e) P - electronegativity decreases down a column as the atomic radius increases

Exercise $3.E.10$**

(a) $\mathrm{C < N < O < F}$

(b) $\mathrm{I < Br < Cl < F}$

(c) $\mathrm{P < S < O < F}$

(d) $\mathrm{Na < Al < P < O}$

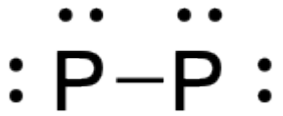
Exercise $3.E.11$**

$\mathrm{O{-}H}$

Exercise $3.E.12$**

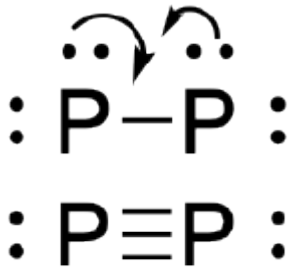
Each P has 5 valence electrons, so a total of 10 valence electrons.

a) $\mathrm{P{-}P}$ 10 - 2 (for bond) = 8 electrons



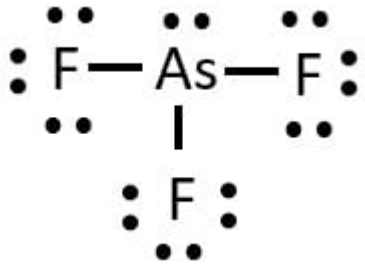
b) Distribute 8 electrons as lone pairs:

c) There are not enough electrons to give each P an octet, so multiple bonds need to be formed. Use one lone pair from each P to form a multiple bond.

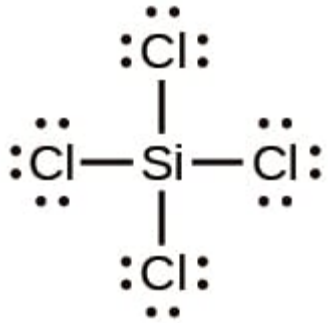


Exercise $3.E.13$**

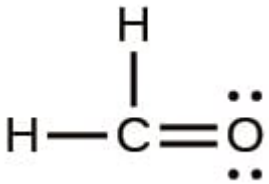
a)



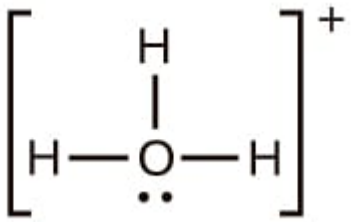
b)



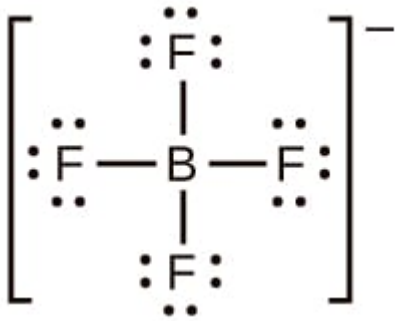
c)



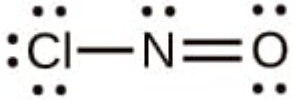
d)



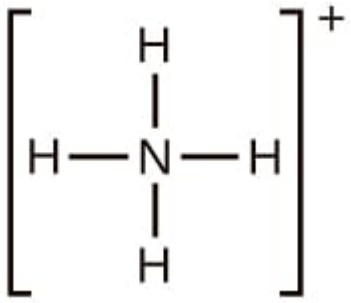
e)



f)



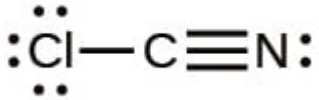
g)



h)



i)

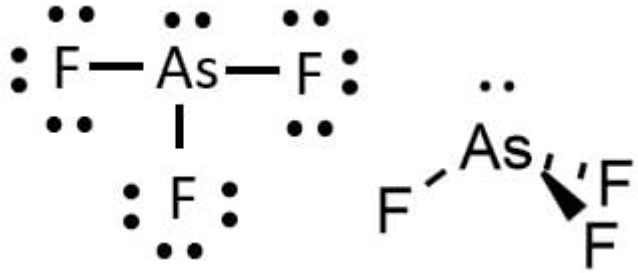


Exercise $3.E.14$*

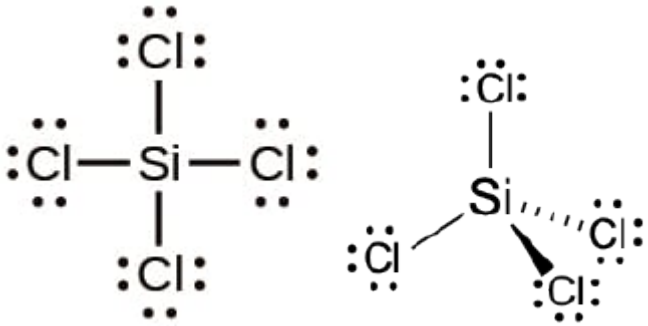
Bonds of each type are formed when electrons are shared between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

Exercise $3.E.15$*

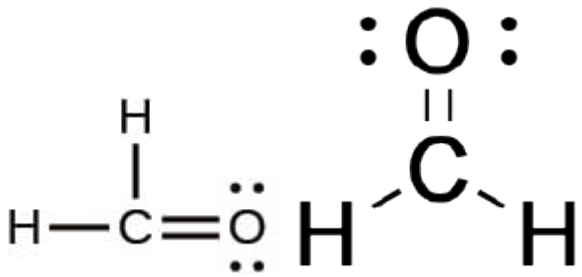
a) The central atom, As, has four electron groups, so the geometry is tetrahedral with ideal bond angles of 109.5°. A lone pair occupies one site, so the shape is trigonal pyramidal.



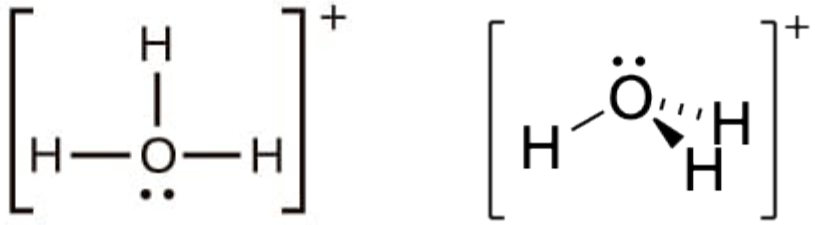
b) The central atom, Si, has four electron groups, so the geometry is tetrahedral with bond angles of 109.5°.



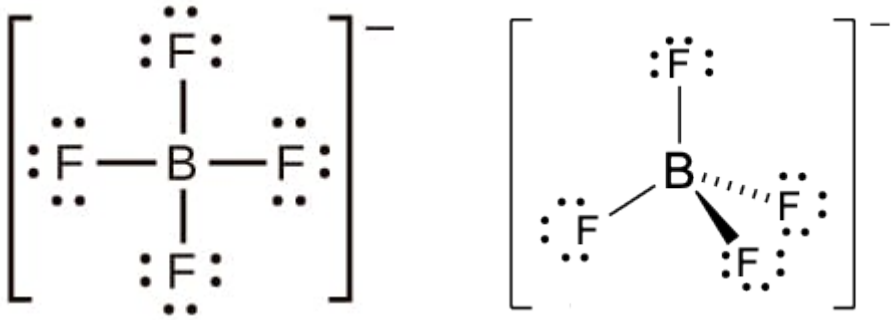
c) The central atom, C, has three electron groups, so the geometry is trigonal planar with ideal bond angles of 120°. (In reality, the four electrons in the double bond repel the two electrons in the single bonds, so the $\mathrm{H-C-O}$ angles are >120° and the $\mathrm{H-C-H}$ angle is <120°.)



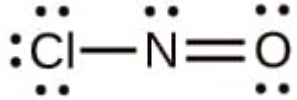
d) The central atom, O, has four electron groups, so the geometry is tetrahedral with ideal bond angles of 109.5°. A lone pair occupies one site, so the shape is trigonal pyramidal.

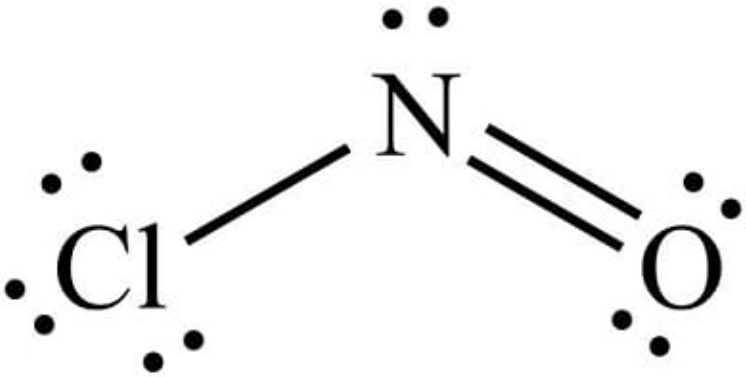


e) The central atom, B, has four electron groups, so the geometry is tetrahedral with bond angles of 109.5°.

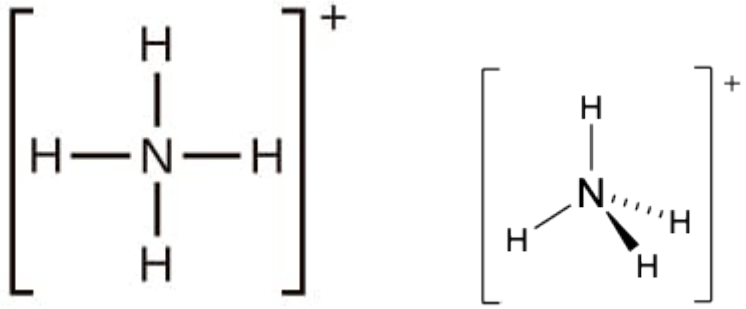


f) The central atom, N, has three electron groups, so the geometry is trigonal planar with ideal bond angles of 120°. A lone pair occupies one site, so the shape is bent.





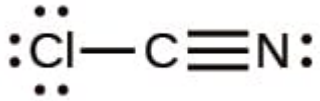
g)The central atom, N, has four electron groups, so the geometry is tetrahedral with bond angles of 109.5°.



h) Each central atom, C, has two electron groups, so the geometry is linear with bond angles of 180°.



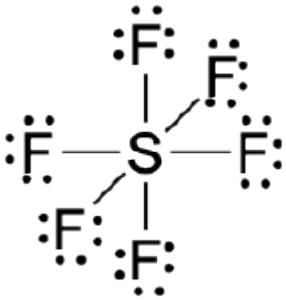
i) The central atom, C, has two electron groups, so the geometry is linear with a bond angle of 180°.



Exercise $3.E.16$**

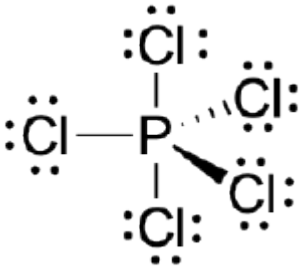
a) First, draw the Lewis structure.

There are 6 + 6 x 7 = 48 total valence electrons. 6 bonds use 12 electrons, leaving 36 electrons. 3 lone pairs on each F use the 36 electrons. S has 6 electron groups, so an octahedral shape.



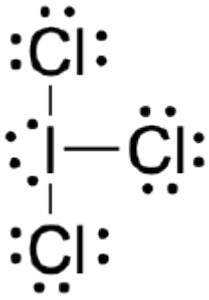
b) First, draw the Lewis structure.

There are 5 + 5 x 7 = 40 total valence electrons. 5 bonds use 10 electrons, leaving 30 electrons. 3 lone pairs on each Cl use the 30 electrons. P has 5 electron groups, so a trigonal bipyramidal shape.



c) First, draw the Lewis structure.

There are 7 + 3 x 7 = 28 total valence electrons. 3 bonds use 6 electrons, leaving 22 electrons. 3 lone pairs on each Cl use 18 electrons, leaving 4 electrons. The remaining electrons form two lone pairs on I. I has 5 electron groups, so a trigonal bipyramidal geometry with lone pairs occupying two sites. This gives a T-shape.



Exercise $3.E.17$*

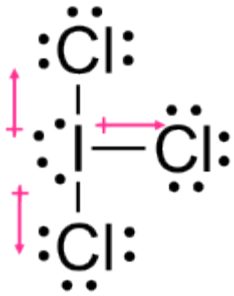
A molecule with polar bonds can be nonpolar if its shape allows the dipole moments to cancel out. For example, in carbon dioxide ($\mathrm{CO_2}$), the linear shape means the polar $\mathrm{C{=}O}$ bonds cancel each other out, making the molecule nonpolar.

Exercise $3.E.18$***

All of these molecules contain polar bonds.

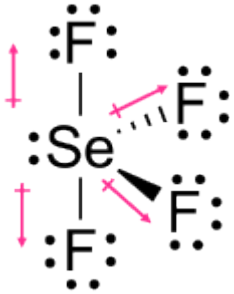
a) $\mathrm{SF_6}$ is an octahedral molecule (see Exercise 16), so the bond dipoles cancel. The molecule does not have a dipole moment.

b) $\mathrm{ICl_3}$ is a T-shaped molecules (see Exercise 16). The bond dipoles do not cancel, so the molecule has a dipole moment.



c) BF_3 has no lone pairs on B, so it has a trigonal planar geometry, so the bond dipoles cancel. The molecule does not have a dipole moment.

d) In drawing the Lewis structure of SeF_4, we see that there is a lone pair on Se. Se, the central atom, therefore has 5 electron groups with a lone pair occupying one site leading to a see-saw shape.

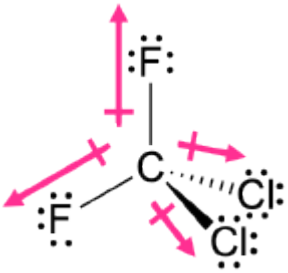


SeF_4 has a dipole moment because the bond dipoles do not cancel.

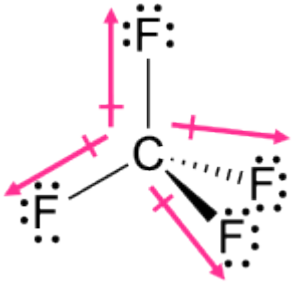
Exercise $3.E.19$***

For each molecule, start by drawing the Lewis structure (with lone pairs!) and determining the geometry of the molecule.

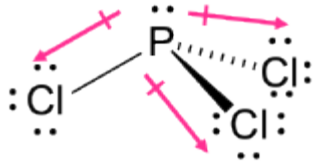
a) The central C has 4 electron groups, giving a tetrahedral geometry. The $C-F$ bond has a larger bond dipole than the $C-Cl$ bonds, due to the larger difference in electronegativity between C and F compared to C and Cl. The molecule has a dipole moment.



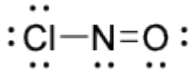
b) This molecule is also tetrahedral, and in this case, the bond dipoles cancel, so the molecule does not have a dipole moment.



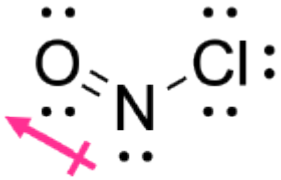
c) PCl_3 has a lone pair on P, so the central atom, P, has four electron groups with one site occupied by a lone pair. This gives a trigonal pyramidal geometry. This molecule has a dipole moment because the bond dipoles do not cancel.



d) From the Lewis structure of ClNO (below), we can see that there is a lone pair on N.



N, the central atom, has three electron groups. Oxygen is more electronegative than N, leading to a polar molecule. Both N and Cl have an electronegativity of 3.0, so the $\mathrm{N-Cl}$ bond is non-polar.



Exercise $3.E.20$*

Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another.

A dipole-dipole attraction is a force that results from the electrostatic attraction of the positive end of one polar molecule to the negative end of another polar molecule

Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond.

Exercise $3.E.21$***

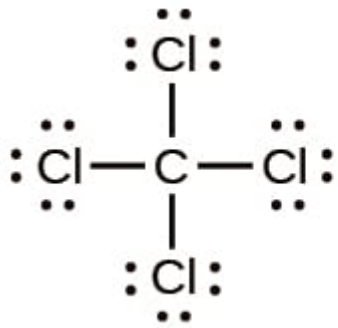
$\mathrm{CH_3CH_2OH}$: hydrogen bonding, dipole-dipole attraction and dispersion forces. Strongest: hydrogen bonding

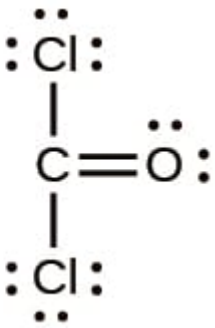
$\mathrm{CH_3CH_2CH_3}$: dispersion forces

$\mathrm{CH_3CH_2Cl}$: dipole-dipole attraction and dispersion forces. Strongest: dipole-dipole

Exercise $3.E.22$***

Consider the Lewis structures of both molecules.





$\mathrm{CCl_4}$ has 4 electron groups about the central atom, so it has a tetrahedral structure and no dipole moment. The only intermolecular force between $\mathrm{CCl_4}$ molecules is dispersion.

Phosgene has three electron groups about the central C atom and thus a trigonal planar shape. Since the electronegativity difference between C and O is greater than that between C and Cl, the molecule has a dipole moment. The intermolecular forces present between phosgene molecules are dispersion and dipole-dipole attractions.

Exercise $3.E.23$**

The dispersion forces typically increase as the number of electrons increases. Therefore, Xe, with the most electrons, has the strongest intermolecular forces and therefore the highest boiling point because it requires the most energy to move the atoms apart to form a gas.

Exercise $3.E.24$**

Although neon (Ne) and hydrogen fluoride (HF) have similar molecular masses, their boiling points differ significantly due to the types of intermolecular forces present in each substance.

The Ne atoms are held together by weak dispersion forces. These are the weakest type of intermolecular force and result from temporary fluctuations in electron

distribution within atoms or molecules.

HF molecules, on the other hand, experience much stronger hydrogen bonding. This makes HF molecules stick together more tightly, requiring more energy (higher temperature) to separate them into a gas phase.

As a result, HF has a much higher boiling point compared to neon.

Exercise $3.E.25$*******

a) As the intermolecular forces in compounds increase, so does the boiling point. H_2O has the strongest intermolecular forces, which are hydrogen-bonding. HCl has dipole-dipole attractions. SiH_4 has only dispersion forces, so the boiling points increase as follows:

$SiH_4 < HCl < H_2O$

b) All of these non-polar diatomic molecules only have dispersion forces. The strength of the dispersion forces increases with the number of electrons, so the boiling points increase as follows:

$F_2 < Cl_2 < Br_2$

Exercise $3.E.26$******

−85 °C. Water has stronger intermolecular forces, hydrogen bonds, so it melts at a higher temperature.

Exercise $3.E.27$******

Acetone cannot have hydrogen bonds between molecules because the hydrogen atoms are covalently bound to C atoms, resulting in non-polar bonds. Propan-1-ol has an $O-H$ bond, and thus, there are hydrogen bonds between the molecules. Since hydrogen bonds are the strongest intermolecular force, propan-1-ol has a higher boiling point.

Exercise $3.E.28$******

a) F, F^-

b) Mg, $Mg_2{}^+$

c) P, $P_3{}^-$

Exercise $3.E.29$*******

For the sulfur to have a partial positive charge, the bond must be with an atom more electronegative than S: N, O, F, and Cl.

Exercise $3.E.30$******

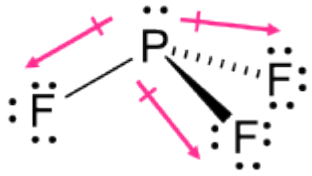
(a) X^-

(b) X^{2-}

(c) X^{2+}

Exercise $3.E.31$*******

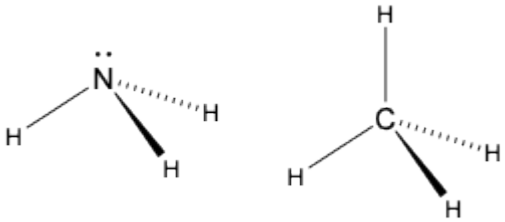
We need to consider whether the central atom has a lone pair. BF_3 does not have a lone pair on B, so the molecule is trigonal planar, so the bond dipoles cancel and the molecule is non-polar. :PF_3 does have a lone pair on the P, so there are 4 electron groups with the lone pairs occupying one site, giving a trigonal pyramidal shape.



X is P.

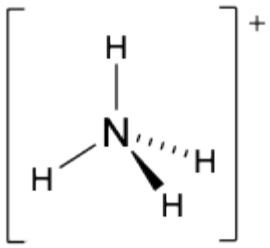
Exercise $3.E.32$*******

a) Consider the Lewis structure for NH_3. The nitrogen has a lone pair, so there are 4 electron groups around the nitrogen atom, giving a tetrahedral geometry with the lone pair occupying one site. CH_4 also has 4 electron groups and a tetrahedral geometry.



The $H-N-H$ bond angles are less than the $H-C-H$ bond angles because the lone pair in NH_3 repels the bonding pairs more strongly, and this increased repulsion pushes the hydrogen atoms closer together, reducing the bond angle.

b) $NH_4{}^+$ has 4 electron groups (with no lone pairs), so the bond angles in the ion are the ideal angles for a tetrahedral geometry, 109.5°, the same as for CH_4.



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4: GASES

4.1: Introduction

4.2: States of Matter

4.3: Pressure

4.4: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

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4.6: Gas Mixtures and Partial Pressures

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4.E: Gases (Exercises)

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

- Thumbnail: As long as black-body radiation (not shown) doesn't escape a system, atoms in thermal agitation undergo essentially elastic collisions. On average, two atoms rebound from each other with the same kinetic energy as before a collision. Five atoms are colored red so their paths of motion are easier to see. (Public Domain; Greg L via Wikipedia)

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4.1: Introduction

Water from Air: A Chemistry Breakthrough for Clean Drinking Water

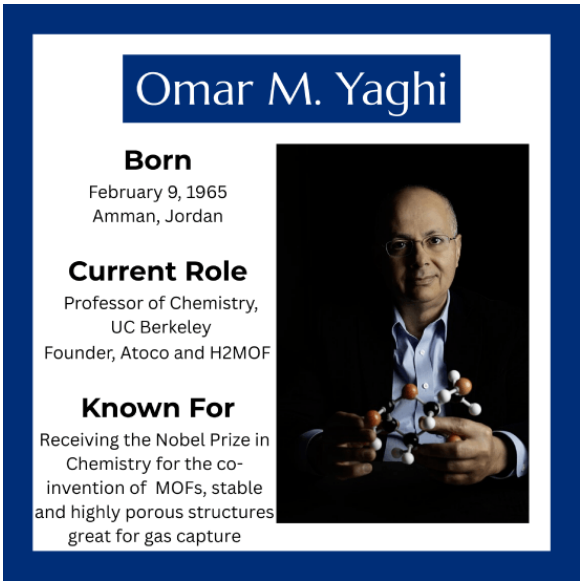


Figure 4.1.1**:** A graphic with basic facts about Omar M. Yaghi, inventor of metal-organic frameworks (MOFs). MOFs have since been used in the applications of greenhouse gas capture, drug delivery, catalysis, and water harvesting. Image from Wikimedia Commons, with permission under Creative Commons license CC-BY.

In this chapter, we'll explore the properties of gases, including how their volume, pressure, temperature, and composition influence their behaviour. One of the most remarkable recent advances in chemistry uses that knowledge to tackle a global challenge: water scarcity.

Chemist Omar M. Yaghi grew up in Jordan, where water was delivered to his neighbourhood only once a week, sometimes for just a few hours. That experience shaped his vision as a scientist: to use chemistry to create new materials that meet basic human needs. In 1995, Yaghi and his lab invented an entirely new class of materials called metal-organic frameworks, or MOFs.

In 2025, Yaghi was awarded the **Nobel Prize in Chemistry**, shared with Susumu Kitagawa and Richard Robson, for developing these groundbreaking materials. MOFs consist of metal ions linked by organic molecules to form porous, crystalline networks with enormous internal surface areas. Their tunable structures make them useful for gas storage, carbon capture, and even water harvesting. The Nobel Prize recognized not only the creativity of this molecular design but also its potential to address global challenges related to clean energy, climate change, and sustainability.

These extended structures (polymers) are made from metal ions connected by organic linkers. MOFs contain vast networks of nanoscopic pores, giving them incredibly high surface areas: a single gram of MOF can have enough surface area to cover a football field. Their size, shape, and chemical composition can be tuned to capture and store specific gas molecules through intermolecular interactions. These gas molecules can later be released by increasing temperature or pressure.

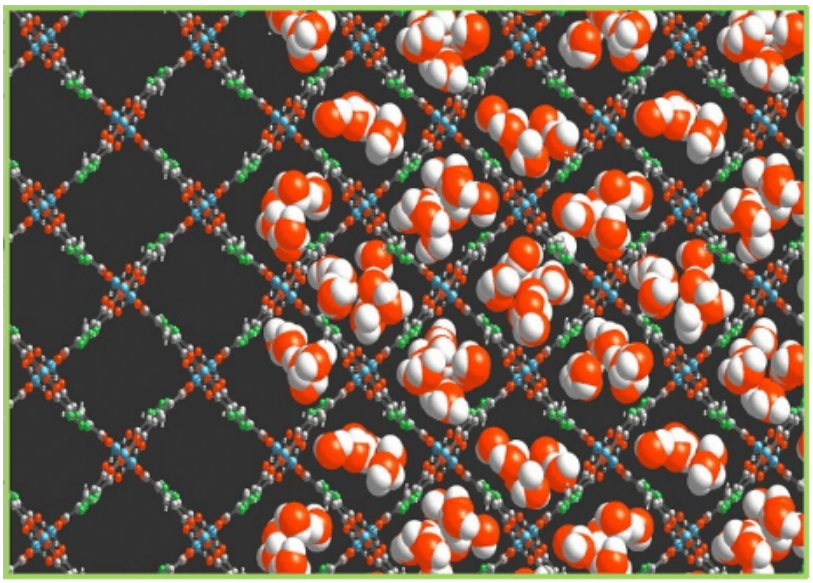


Figure 4.1.2**:** Illustration of a MOF framework that demonstrates how water molecules can be entrapped in the structure's nanopores. Adapted from Xu and Yaghi, *ACS Central Science* **2020**, 6(8) with permission under Creative Commons license CC-BY; copyright 2020 American Chemical Society.

MOFs were originally designed to store gases like hydrogen and capture carbon dioxide from industrial emissions, but in 2014 Yaghi's team discovered that certain MOFs also absorbed water vapour from the air, even in very dry conditions. This inspired Yaghi to develop MOFs specifically for harvesting water from air. Yaghi's team built a simple prototype: an inner box containing a MOF called MOF-801, nested inside a lidded outer box. At night, the lid opened to expose the MOF to the air for water capture; during the day, it closed to trap heat from the sun. The rise in temperature caused the MOF to release the captured water vapour, which condensed inside the box and was collected as liquid water. In the Mojave Desert, this device harvested up to 1L of drinkable water per kilogram of MOF per day, using only ambient temperature and pressure, no electricity required.

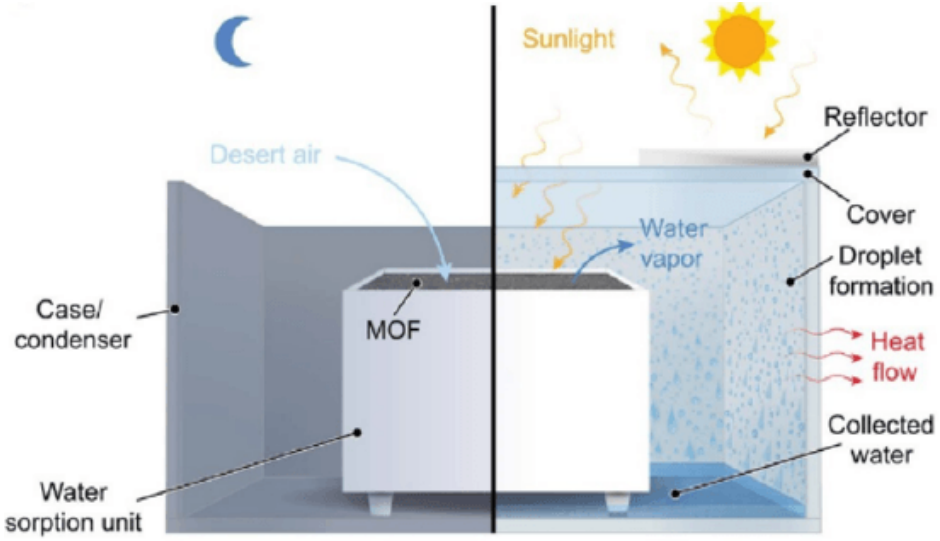


Figure 4.1.3**:** An illustration of the simple device used by Yaghi and his team for water harvesting from desert air under ambient temperature and pressure. The nighttime configuration for water vapour collection by the MOF exposed to open air is shown on the left. On the right, the daytime configuration is shown. The lid of the outer box is on so that heat from the sunlight causes vapour release, condensation, and liquid water collection. Adapted from Dao, Chien, and Strek *VNUHCM Journal of Science and Technology Development* **2020**, *23(2)* with permission under Creative Commons license CC-BY.

Yaghi's team has since developed improved MOFs like MOF-303 and partnered with companies to scale up production. With further optimization, these materials could produce tens of litres per kilogram of MOF per day, offering a low-cost, low-energy

source of renewable freshwater, even in arid regions. Thirty years after his first MOF paper, Yaghi's vision is helping meet one of the most fundamental needs of life through his water harvesting technology.

While the development of MOFs is rooted in materials chemistry, their ability to trap and release gas molecules depends on temperature, pressure, and other gas properties. In this chapter, we explore the principles that help us describe and predict gas behaviour.

Glossary

Nobel Prize in Chemistry

A prestigious international award recognizing groundbreaking contributions to the field of chemistry.

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4.2: States of Matter

Learning Objectives

- Describe the properties of the solids, liquids, and gases

The three common phases (or states) of matter are gases, liquids, and solids.

Gases have the lowest density of the three states. They are highly compressible and expand to completely fill any container. Because the intermolecular forces in gases are weak compared to the kinetic energy of the particles, the particles move freely and remain far apart from one another.

Solids, in contrast, are dense, rigid, and incompressible. Their strong intermolecular forces keep the particles locked in fixed positions, allowing only slight vibrations. As a result, solids maintain a definite shape and volume.

Liquids share some characteristics of both solids and gases. Like solids, they are dense and incompressible, but unlike solids, their particles can move past one another, allowing them to flow and take the shape of their container. The strength of the intermolecular forces relative to the kinetic energy in liquids is stronger than in gases but weaker than in solids. As a result, liquid particles remain close together, they are not fixed in place.

Figure 4.2.1 illustrates the molecular differences between gases, liquids and solids using oxygen, O_2, as an example:

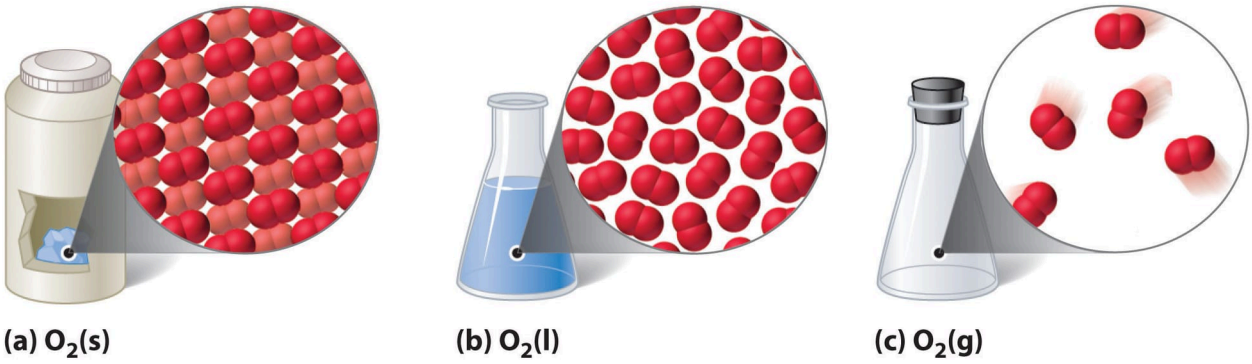


Figure 4.2.1: O_2 in the Solid, Liquid, and Gaseous States: (a) Solid oxygen has a fixed shape and volume, with its molecules packed tightly together. (b) Liquid oxygen takes the shape of its container but maintains a fixed volume, with its molecules remaining relatively close to one another. (c) Gaseous oxygen expands to fill any container and consists of widely separated molecules that move independently.

The physical state of a substance depends on temperature and pressure. Water is a familiar example of a substance that exists in all three states under everyday conditions. Solid water, or ice, is found in snow, ice cubes, and glaciers. Liquid water is the most common and essential form, present in lakes, rivers, and oceans, as well as in drinking water. Water also exists as a gas, known as water vapor, which is part of the air we breathe and forms when water evaporates, such as from boiling water or drying clothes.

Although the individual water molecules (H_2O) are identical in all states, the macroscopic properties of water, such as density, volume and compressibility, depend on interactions between molecules (intermolecular forces) and external conditions, such as temperature and pressure.

For your interest, Figure 4.2.2 shows elements commonly found in the gaseous, liquid, and solid states at 25°C and 1.0 atm. . Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. The noble gases (group 18) exist as monatomic gases, while the other gaseous elements, hydrogen, nitrogen, oxygen, fluorine, and chlorine, are diatomic

molecules. Oxygen can also form a second allotrope, ozone (O_3), a highly reactive triatomic gas. In contrast, bromine (Br_2) and mercury (Hg) are liquids at 25°C and 1.0 atm. The remaining elements are all solids under these conditions.

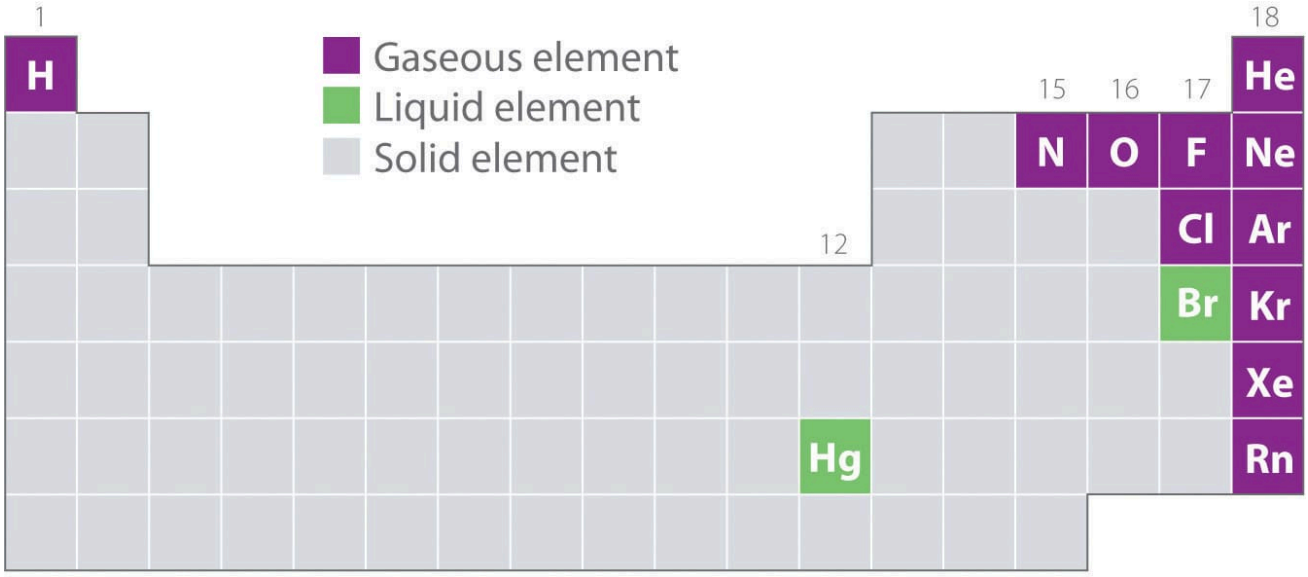


Figure 4.2.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

Gaseous elements are shown in purple, liquids in green, and solids in gray.

Summary

Matter exists in three states: gas, liquid, and solid. Gas particles are far apart, making gases highly compressible. Gases expand to fill their container. Liquid particles are close together, making liquids dense and relatively incompressible, but they can move past each other, allowing liquids to take the shape of their container. The particles of solids are close together and vibrate in fixed positions, making solids dense, rigid, and incompressible.

The physical state of a substance depends on the balance between intermolecular forces and the kinetic energy of the particles, which is determined by both temperature and pressure.

Glossary

gas
: State in which matter has neither definite volume nor shape.

liquid
: State of matter that has a definite volume but indefinite shape.

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

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4.3: Pressure

Learning Objectives

- Describe the pressure of a gas.
- Determine the pressure of a gas from a manometer or barometer
- Convert between units of pressure.

To fully describe a gas sample, we need four measurable quantities:

- temperature (in Kelvins),
- volume (in liters),
- amount (in moles),
- pressure (in atmospheres)

These variables are not independent, meaning that changing one affects the others. If we know three of these values, we can calculate the fourth, giving us a complete physical description of the gas. This section focuses on pressure and how it is measured.

What is Pressure?

When you inflate a balloon, you can feel the air inside pushing against its surface. This happens because gases, like all forms of matter, exert force on the surfaces they touch. A basketball filled with air feels firm because of the force of the collisions of the gas particles against the inner walls. Solid objects, like a book resting on a table, exert gravitational force due to their weight.

Pressure (P) depends on both the force (F) applied and the area (A) over which the force is distributed:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{4.3.1}$$

The same force applied to a smaller area creates a higher pressure. For example, when using a garden hose, placing a thumb over the opening reduces the area where the water exits. This increases the pressure, making the water spray more forcefully.

The units of pressure come from the units used to measure force and area. In the International System of Units (SI), force is measured in newtons (N), and area in square meters (m^2). The standard SI unit for pressure is the pascal (Pa), which is defined as one newton per square meter:

$$1\ \text{Pa} = 1\ \text{N/m}^2$$

Atmospheric Pressure

Just as we exert pressure on a surface due to gravity, so do the gases in our atmosphere. The weight of the air above us creates atmospheric pressure, which is substantial. A 1 m^2 column of air, extending from sea level to the top of the atmosphere, has a mass of about 10,000 kg, resulting in a pressure of approximately 101 kPa:

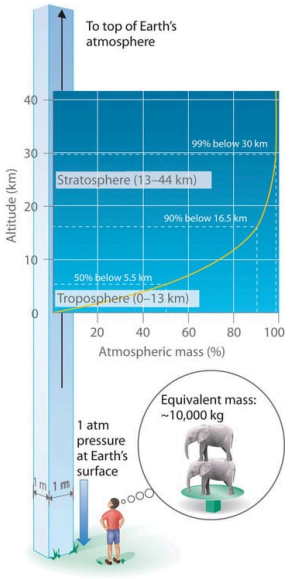


Figure 4.3.1: Atmospheric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

At sea level, this pressure is equivalent to the weight of a full-grown elephant standing on a doormat or a bowling ball pressing on your thumbnail. Although these comparisons make atmospheric pressure seem immense, life on Earth has evolved under these conditions, so we do not feel the weight of the air around us.

A dramatic demonstration of atmospheric pressure can be seen in this brief video of a railway tanker car imploding. The tanker collapses when its internal pressure is reduced, allowing the much greater atmospheric pressure outside to crush it:



Measuring Atmospheric Pressure: The Barometer

Atmospheric pressure can be measured using a barometer, a device invented in 1643 by Evangelista Torricelli, a student of Galileo. A barometer consists of a long glass tube, sealed at one end, filled with mercury, and inverted into a dish of mercury without allowing air to enter the tube. Some mercury flows out, but a tall column remains inside (Figure 4.3.2).

Why doesn't all the mercury drain from the tube? The answer lies in the balance of forces. Gravity pulls the mercury in the column down, but atmospheric pressure pushes on the surface of the mercury in the dish, forcing mercury up into the tube. Because the space above the mercury column is a vacuum, there is no air pressure inside the tube to push down on the mercury. The column

settles at a height where the pressure from the downward force of gravity on the mercury column in the tube exactly balances the pressure of the atmosphere pushing on the Mercury in the dish:

$$P_{atmosphere} = P_{HgColumn}$$

The pressure from the Mercury column can be described by the ratio of the gravitational force acting on its mass (F_g) and the area at the bottom of the tube (A). With further manipulation, we can see that atmospheric pressure can be described from a manometer using only the density of the liquid in the tube (ρ), the gravitational acceleration constant (g), and the height of the column (h):

$$\begin{aligned} P_{atmosphere} &= \frac{F_g}{A} \\ &= \frac{m \cdot g}{A} \\ &= \frac{\rho \cdot V \cdot g}{A} \\ &= \frac{\rho \cdot A \cdot h \cdot g}{A} \\ &= \rho g h \end{aligned}$$

- F_g gravitational force acting on the Mercury column,
- A is the area at the bottom of the tube,
- m is the mass of the Mercury column in the tube,
- g is the gravitational acceleration constant,
- V is the volume of the Mercury column in the tube,
- ρ is the density of Mercury, and
- h is height of the Mercury column.

While we will not calculate the height of mercury columns in CHM 135H, these equations show that the density of the liquid in a barometer affects the height of the column. Mercury is used because of its high density (13.6 g/cm^3), which keeps the column height manageable. If a less dense liquid like water were used, the column would have to be over 10 meters tall to balance atmospheric pressure.

Under normal weather conditions at sea level, the mercury column reaches a height of approximately 760 mm above the level of mercury in the dish (Figure 4.3.2). This value changes with weather patterns and altitude, which is why barometers are useful for tracking atmospheric pressure changes and predicting weather conditions.

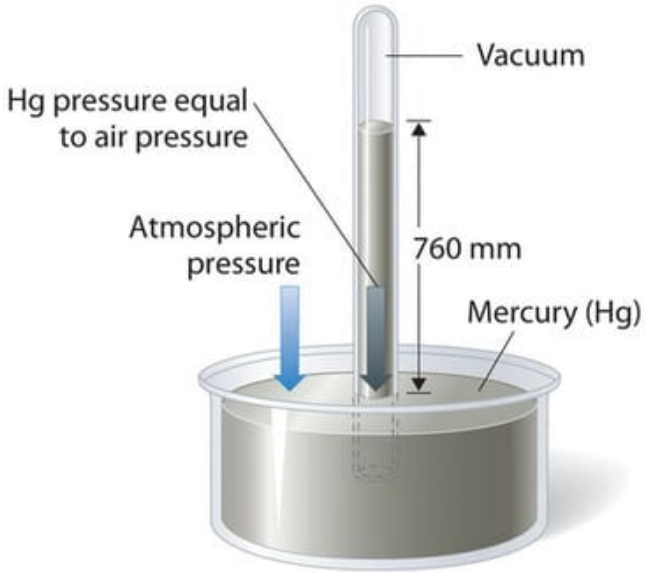


Figure 4.3.2: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall.

Mercury barometers have been used to measure atmospheric pressure for centuries, leading to the development of a specific pressure unit: the millimeter of mercury (mmHg), also called the torr in honor of Torricelli. Standard atmospheric pressure is defined as the pressure required to support a 760 mm column of mercury in a barometer. This pressure is also known as 1 atmosphere (atm).

The atmosphere (atm) is commonly used in chemistry, but pressure can also be expressed in other units. The relationships between these units are:

$$\begin{aligned} 1 \text{ atm} &= 760\ mmHg \\ &= 760\ torr \\ &= 1.01325 \times 10^5\ Pa \\ &= 101.325\ kPa \end{aligned}$$

Thus, a pressure of 1 atm is exactly 760 mmHg.

We rarely notice the absolute value of atmospheric pressure because we are constantly surrounded by it. However, we do feel changes in pressure, such as when our ears pop during rapid changes in altitude—like when riding a fast elevator, flying in an airplane, or driving through mountains. These pressure shifts cause the air inside our ears to adjust, making us more aware of the surrounding pressure.

Example 4.3.1: Conversion of Pressure Units

A typical pressure in Toronto is 1.01 atm. What is this pressure in millimeters of mercury?

Solution

This is a unit conversion problem. 1 atm = 760 mmHg

$$1.01 \text{ atm} \left(\frac{760 \text{mmHg}}{1 \text{ atm}} \right) = 768 \text{mmHg}$$

Exercise 4.3.1: Pressure Units

Mt. Logan, at 5959 m above sea level, is Canada's tallest mountain. The normal barometric pressure at this altitude is about 360 mmHg. Convert this pressure to atm.

Answer available at the end of this section.

Manometers

A manometer is a device used to measure the pressure of a gas trapped in a container. It works similarly to a barometer but is specifically designed to measure the pressure of a gas sample. The key component of a manometer is a U-shaped tube containing mercury (or another nonvolatile liquid).

There are two types of manometers: closed-end and open-end.

A closed-end manometer, shown in Figure 4.3.3a, has one end of the U-tube sealed. When no gas is present in the bulb, the heights of the mercury columns in both arms are equal because the space above the mercury in the sealed arm is a vacuum (containing only traces of mercury vapor). When a gas is introduced into the bulb, it exerts pressure on the mercury in the right column, causing the two columns to have different heights. The difference in height directly represents the pressure of the gas in the bulb.

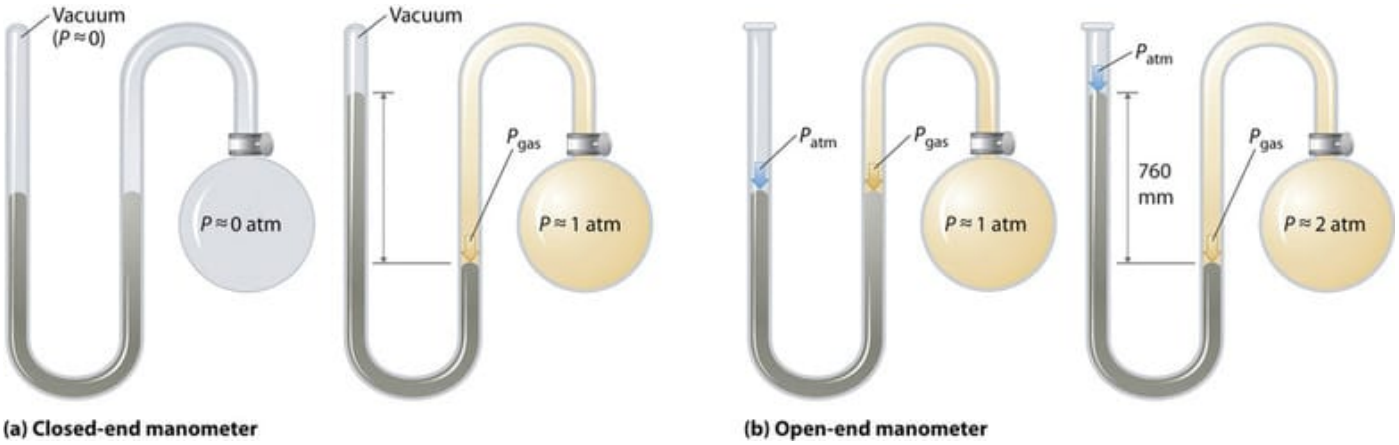


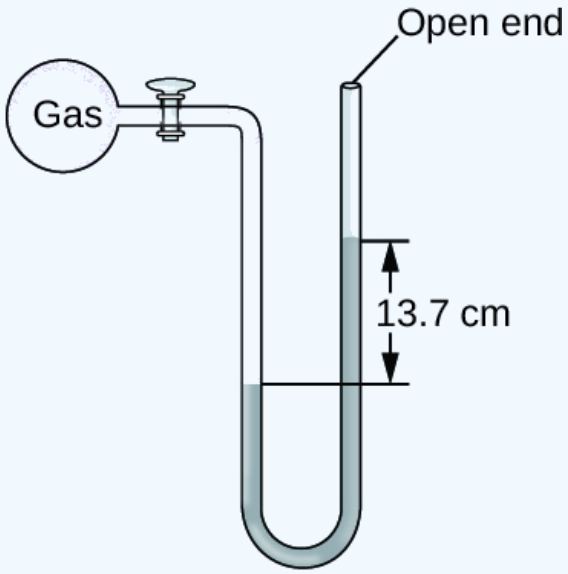
Figure 4.3.3: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1$ atm), and the difference in the heights of the two columns gives the *difference* between atmospheric pressure and the pressure of the gas in the bulb.

An open-end manometer, shown in Figure 4.3.3b, has one end of the U-tube open to the atmosphere. The behavior of the mercury column depends on the relationship between the gas pressure in the bulb and atmospheric pressure:

- If the gas pressure inside the bulb is equal to atmospheric pressure, the mercury levels in both arms will be the same.
- If the gas pressure inside the bulb is greater than atmospheric pressure, the gas pushes the mercury down in the arm connected to the bulb, raising the mercury level in the open arm. The gas pressure is calculated as atmospheric pressure plus the height difference between the two mercury levels.
- If the gas pressure inside the bulb is lower than atmospheric pressure, the mercury level in the bulb-connected arm will be higher than in the open arm. In this case, the gas pressure is calculated as atmospheric pressure minus the height difference.

Example 4.3.2: 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. Atmospheric pressure is 760 mmHg. Determine the pressure of the gas in mmHg and atm.



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 13.7 centimeters. The level on the right side is higher than on the left.

Solution

The pressure of the gas equals the pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level.

Convert 13.7 cm to mm.

$$13.7\text{cm}\left(\frac{10\text{ mm}}{\text{cm}}\right) = 137\text{ mm}$$

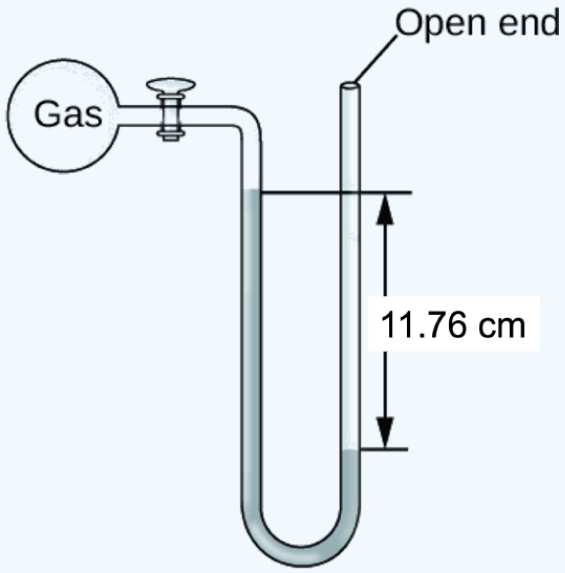
Since the level of the mercury is lower at the gas side of the U-tube, the gas pressure is greater than atmospheric pressure.

P_{gas} = 137 mmHg + 760 mmHg = 897 mmHg.

$$897\ \cancel{\text{mmHg}} \times \frac{1\text{ atm}}{760\ \cancel{\text{mmHg}}} = 1.18\text{ atm}$$

Exercise 4.3.2

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 mmHg and atm.



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 11.76 cm. The level on the left side is higher than the right.

Answer available at the end of this section.

Chemistry in Everyday Life: Measuring Blood Pressure

Blood pressure is measured using a sphygmomanometer, a device that consists of an inflatable cuff, a manometer to measure pressure, and a method to detect blood flow. Invented in 1881, it remains a vital medical tool for assessing cardiovascular health (Figure ({4{.}3{.}\eatSpaces{4} \endSpaces})).

To measure blood pressure, the cuff is wrapped around the upper arm and inflated until it temporarily stops blood flow. As the cuff slowly deflates, blood begins to flow again, and two key pressure measurements are recorded.

The systolic pressure is the highest pressure in the arteries, occurring when the heart beats and pushes blood through the circulatory system. When the cuff's pressure drops to match the systolic pressure, blood starts flowing past the cuff, producing sounds that can be heard through a stethoscope. This is the first reading on the gauge.

The diastolic pressure is the lowest pressure, occurring when the heart is at rest between beats. As the cuff deflates further, blood flow returns to normal, and the sound of pulsing blood fades. The pressure at this moment represents the diastolic pressure, which is recorded as the second reading.

Blood pressure is expressed in millimeters of mercury (mmHg), reflecting the historical use of mercury-based manometers in medical instruments. A typical healthy blood pressure reading is 120/80 mmHg, where 120 mmHg is the systolic pressure and 80 mmHg is the diastolic pressure.

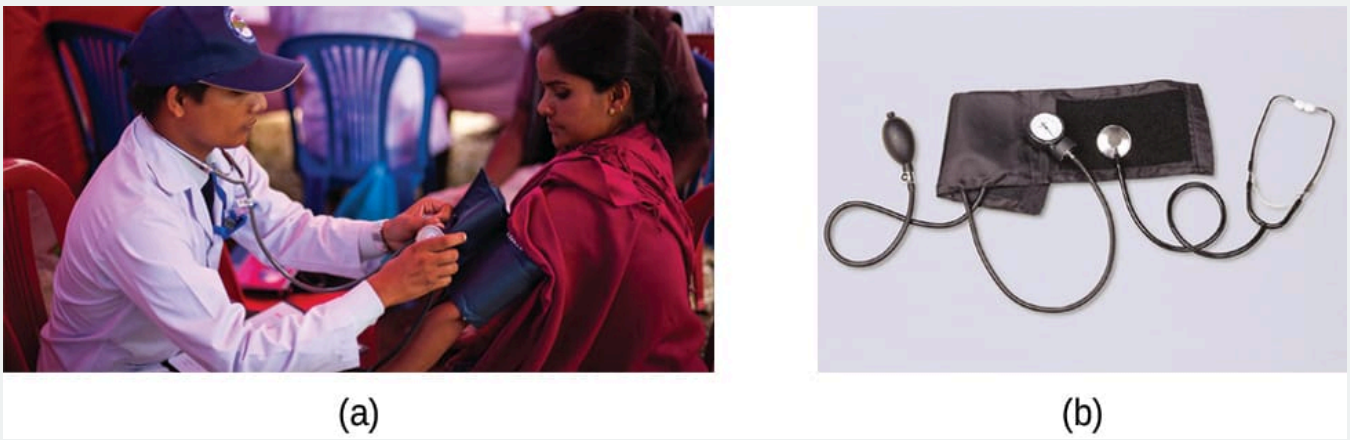


Figure 4.3.4: (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

Summary

A complete description of a gas sample requires four measurable quantities: temperature, volume, amount, and pressure. Pressure is defined as force per unit area, with the SI unit being the pascal (Pa), where 1 Pa = 1 N/m^2. The pressure exerted by an object is proportional to the force it applies and inversely proportional to the area on which the force is distributed.

The pressure exerted by Earth's atmosphere, known as atmospheric pressure, is approximately 101 kPa (1 atm) at sea level. It is commonly measured using a barometer, a closed, inverted mercury-filled tube, where the height of the mercury column corresponds to atmospheric pressure. This pressure is often reported in millimeters of mercury (mmHg), also called torr.

A manometer is used to measure the pressure of a gas sample. A closed-end manometer directly measures gas pressure relative to a vacuum, while an open-end manometer compares gas pressure to atmospheric pressure, adjusting for differences in column height.

Glossary

atmosphere (atm)
: Unit of pressure; 1 atm = 101,325 Pa.

atmospheric pressure
: The pressure exerted by the gases in Earth's atmosphere; approximately 101 kPa (1 atm) at sea level.

barometer
: Device used to measure atmospheric pressure in millimeters of mercury (mmHg) or torr.

manometer
: Device used to measure the pressure of a gas trapped in a container, either relative to a vacuum (closed-end) or to atmospheric pressure (open-end).

pascal (Pa)
: The SI unit of pressure; 1 Pa = 1 N/m^2.

pressure
: Force exerted per unit area.

torr
: Unit of pressure; 1 torr = 1/760 atm.

Answers

Exercise 4.3.1: Pressure Units

0.47 atm

Exercise 4.3.2

642 mmHg, 0.845 atm

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4.4: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

Learning Objectives

- Describe the mathematical relationships between the key properties of gases: pressure, volume, temperature, and amount (moles).
- Apply the ideal gas equation to calculate and convert between pressure, volume, moles, and temperature of a gas.

Early scientists investigated how the macroscopic properties of gases—pressure (P), temperature (T), volume (V), and amount (n)—are related. To do this, they designed experiments where they kept two properties constant, changed a third, and measured the effect on the fourth. For example, they might keep the amount of gas and temperature constant, change the pressure, and observe how the volume responds.

By studying different combinations of these variables, scientists discovered mathematical relationships between pairs of gas properties, such as pressure and temperature or pressure and volume. These relationships describe an ideal gas, a theoretical model that real gases approximate under many conditions.

Eventually, these separate gas laws were combined into a single equation called the ideal gas equation, which describes the behaviour of gases at low pressures and moderate temperatures. In this section, we will explore the individual relationships between gas properties and see how they combine to form the ideal gas law.

Pressure and Temperature

Consider a rigid, sealed container filled with gas and connected to a pressure gauge. Because the volume and the amount of gas remain constant, the only variables that change are temperature and pressure.

When the gas is cooled, its pressure decreases. When the gas is heated, its temperature increases, and so does its pressure. This effect is demonstrated in Figure 4.4.1, which shows how a gas in a rigid container behaves at different temperatures.

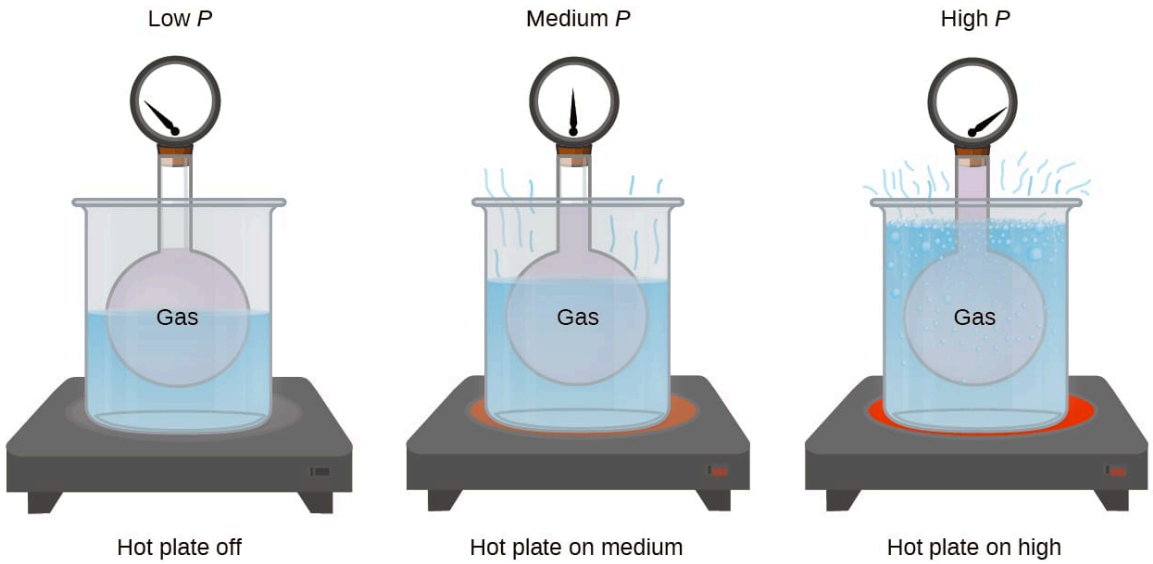


Figure 4.4.1: The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the container is relatively low. As the gas is heated, the pressure of the gas increases.

The direct relationship between temperature and pressure is observed for any gas confined to a constant volume. Experimental

data for a sample of air under these conditions is shown in Figure 4.4.2.

Temperature (°C)	Temperature (K)	Pressure (kPa)
-100	173	36.0
-50	223	46.4
0	273	56.7
50	323	67.1
100	373	77.5
150	423	88.0

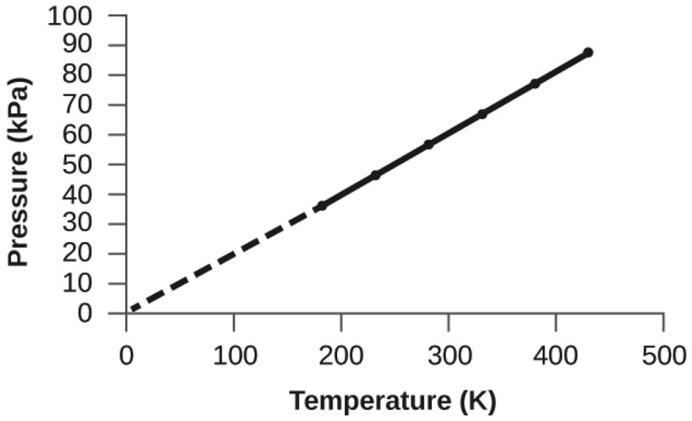


Figure 4.4.2: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is measured in Kelvin. When this line is extrapolated to lower pressures, the pressure reaches 0 at –273 °C, which is 0 on the Kelvin scale and the lowest possible temperature, known as absolute zero.

When volume is constant, the pressure of a given amount of gas is directly proportional to the temperature (measured in Kelvin). This means that if the temperature on the Kelvin scale increases by a certain factor, the gas pressure increases by the same factor, as long as the volume and amount of gas remain constant. Mathematically, this can be written as:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where $\propto$ means "is proportional to," and *k* is a proportionality constant that depends on the identity, amount, and volume of the gas.

Volume and Temperature

Imagine a sealed balloon at atmospheric pressure (1 atm). If the balloon is put in a refrigerator, the gas inside cools and the balloon shrinks, even though the amount of gas and its pressure remain constant. If the balloon gets very cold, the volume of the balloon will decrease significantly. When the balloon is warmed again, it expands back to its original size.



Figure 4.4.3: When the amount of gas and the pressure are held constant, the volume increases when temperature is increased.

(CC BY-SA-NC; anonymous).

This demonstrates a fundamental principle: for a fixed amount of gas at constant pressure, temperature and volume are directly proportional. Experimental data for a 1-mole sample of methane gas at 1 atm confirm this pattern, as shown in Figure 4.4.4.

Temperature (°C)	Temperature (K)	Volume (L)
−3	270	22
−23	250	21
−53	220	18
−162	111	9

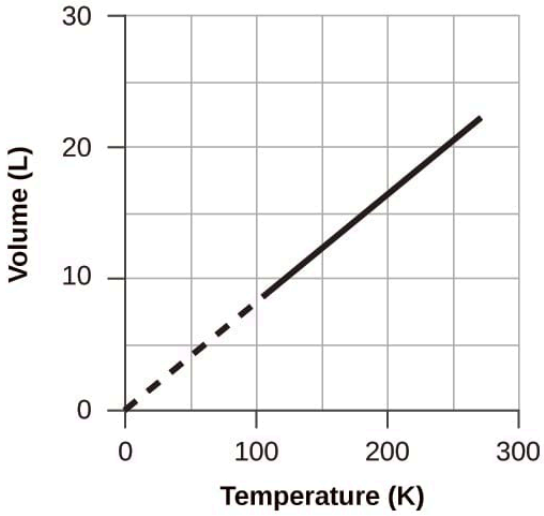


Figure 4.4.4: The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in Kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The 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:

$$V \propto T \text{ or } V = \text{constant} \times T \text{ or } V = k \times T$$

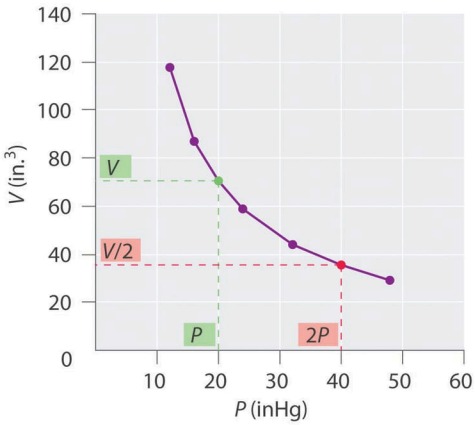
with *k* being a proportionality constant that depends on the amount and pressure of the gas.

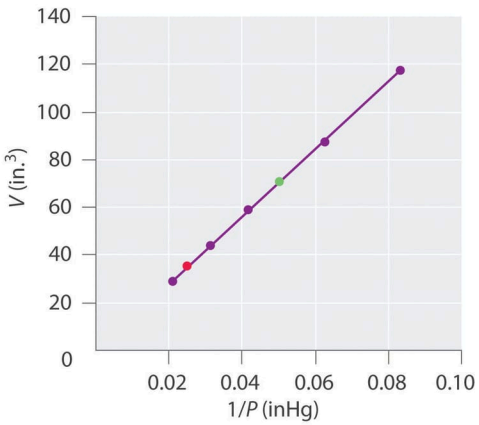
Volume and Pressure

Consider an airtight syringe filled with air at a constant temperature. If you slowly push in the plunger, the gas inside is compressed into a smaller volume, causing its pressure to increase. Conversely, if you pull out the plunger, the volume expands and the pressure decreases. This demonstrates the fundamental relationship between volume and pressure for a confined gas: decreasing volume increases pressure, while increasing volume decreases pressure.

One of the first scientists to study this relationship quantitatively was the Irish chemist Robert Boyle (1627–1691). His experiments showed that for a fixed amount of gas at constant temperature, pressure and volume are inversely proportional (Figure 4.4.5).

P (inHg)	*V* (in.^{3})	*PV*
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400





(a) Data from Boyle's experiment **(b) Volume vs. pressure** **(c) Volume vs. 1/pressure**

Figure 4.4.5: Plots of Boyle's Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because *PV* is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation *V* = constant/*P* (CC BY-SA-NC; anonymous).

Unlike pressure-temperature and volume-temperature relationships, pressure and volume are not directly proportional. Instead, they are inversely proportional: increasing pressure reduces volume, and decreasing pressure increases volume. This relationship is mathematically expressed as:

$$P \propto \frac{1}{V}$$

or

$$P = k \cdot \frac{1}{V}$$

where k is a constant. When plotted, volume vs. pressure forms a curved (hyperbolic) graph, while volume vs. 1/P produces a straight-line graph (Figure 4.4.5). Scientists often prefer linearized data because straight-line graphs make it easier to interpret trends and fit experimental data to theoretical models.

Chemistry and Everyday Life: Breathing

The relationship between volume and pressure is essential to breathing. Your lungs function as a gas exchange system, bringing in oxygen and expelling carbon dioxide. Made of spongy, elastic tissue, the lungs expand and contract with each breath, following the principles of pressure and volume changes.

When you inhale, the diaphragm contracts and moves downward, while the intercostal muscles (muscles between your ribs) expand the chest cavity. This increase in lung volume causes a decrease in air pressure inside the lungs. Since air naturally moves from high pressure to low pressure, air flows into the lungs.

When you exhale, the process reverses. The diaphragm and rib muscles relax, reducing the chest cavity size and decreasing lung volume. This causes lung pressure to increase, forcing air out of the lungs (Figure 4.4.6).

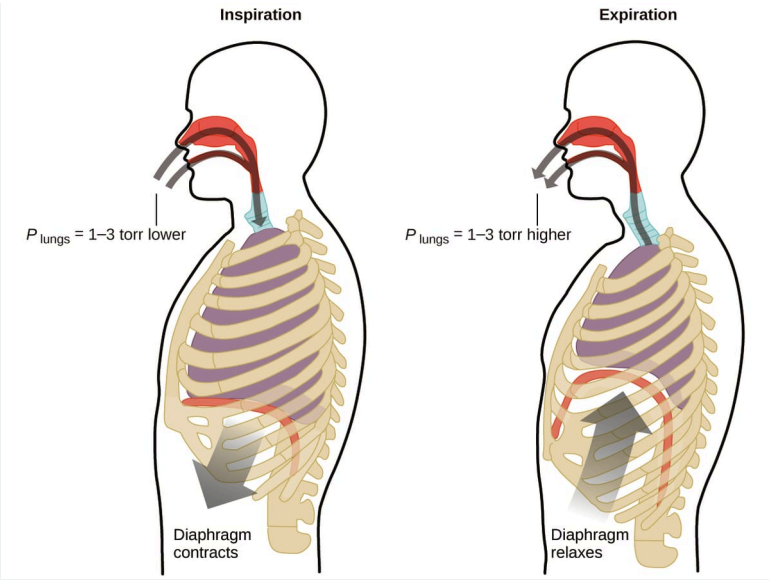
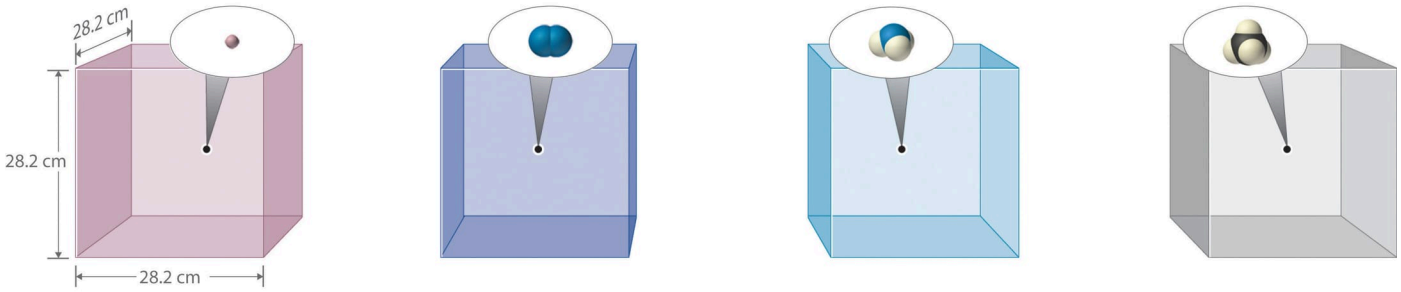


Figure 4.4.6: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

Volume and Moles of Gas

Experimental evidence supports the observation that the volume of a gas is directly proportional to the number of moles (n) of gas present, irrespective of the nature of the gas (e.g. it's molar mass), provided that pressure and temperature remain constant. You experience this relationship when you blow up a balloon. You are adding moles of gas to the ballon as you blow and the volume of the balloon is increasing. Mathematically, this relationship is expressed as:

$$V \propto n \text{ or } V = k \times n$$



He
$V = 22.4$ L
$P = 1$ atm
$T = 0$°C
Mass: 4.003 g/mol
n = 1 mol

N_2
$V = 22.4$ L
$P = 1$ atm
$T = 0$°C
Mass: 28.013 g/mol
n = 1 mol

NH_3
$V = 22.4$ L
$P = 1$ atm
$T = 0$°C
Mass: 17.031 g/mol
n = 1 mol

CH_4
$V = 22.4$ L
$P = 1$ atm
$T = 0$°C
Mass: 16.043 g/mol
n = 1 mol

Figure 4.4.7: Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the mass of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

The Ideal Gas Law

So far, we have examined four separate gas laws that describe the relationships between pressure, volume, temperature, and the number of moles of gas:

- PV = constant at fixed T and n
- $\frac{P}{T}$ = constant at fixed V and n
- $\frac{V}{T}$ = constant at fixed P and n
- $\frac{V}{n}$ = constant at fixed P and T

By combining these four relationships, scientists derived a single equation that describes the behaviour of gases under most conditions:

$$PV = nRT \tag{4.4.1}$$

where:

- P = pressure of a gas (atm)
- V = volume (L)
- n = number of moles of the gas
- T = temperature (K)
- R = universal gas constant,

The value of R depends on the units used for pressure and volume. When pressure is measured in atmospheres (atm), volume in litres (L), and temperature in Kelvin (K), then:
$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$

An ideal gas is a hypothetical gas that behaves exactly as predicted by the ideal gas law. In reality, no gas is truly "ideal", but the ideal gas model provides a useful approximation under most conditions. At low pressures and moderate temperatures, real gases behave similarly to ideal gases, making the ideal gas equation a valuable tool for predicting gas behaviour. However, at very high pressures or very low temperatures, real gases deviate from ideal behavior due to intermolecular forces and the finite size of gas particles.

Example 4.4.1: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of the methane gas at 25 °C and 745 torr?

Solution

Rearrange $PV = nRT$ to solve for V:

$$V = \frac{nRT}{P}$$

Given the units of R (0.08206 L atm mol^{-1} K^{-1}), we need to convert the temperature to Kelvin and the pressure to atm.

Converting into the units consistent with R:

$$n = 655 \ \cancel{\text{g CH}_4} \times \frac{1 \text{ mol}}{16.04 \ \cancel{\text{g CH}_4}} = 40.8 \text{ mol}$$

$$T = 25^\circ C + 273 = 298 \text{ K}$$

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \ \cancel{\text{mol}}) \left(0.08206 \ L \ \cancel{\text{atm mol}^{-1}\text{K}^{-1}}\right) (298 \ \cancel{K})}{0.980 \ \cancel{\text{atm}}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It would require a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Exercise 4.4.1

Calculate the pressure in atm of 2520 moles of hydrogen gas stored at 27 °C in the 180.0 L storage tank of a modern hydrogen-powered car.

Answer available at the end of this section.

Example 4.4.2

Following the recognition of hydrochlorofluorocarbon (CFC) refrigerants as ozone depleting substances, chemists searched for more sustainable alternatives. Hydrofluorocarbons (HFCs) replaced CFCs as they were found to have lower ozone depletion potentials. Two commonly used hydrofluorocarbons are 1,1,1,2-tetrafluoroethane ($C_2H_2F_4$) and 1,1,1,2,2,3-hexafluoropropane ($C_3H_2F_6$).

A standard air-conditioning unit at 25 °C contains 70.0 L of refrigerant gas at 8.00 atm before the unit is turned on. For both refrigerants, what is the mass contained in the air conditioning unit?

Solution

Calculate the moles of refrigerant gas in the unit:

$$n = \frac{PV}{RT} = \frac{(8.00\text{ atm})(70.0\text{ L})}{(298.15\text{ K})(0.08206\frac{\text{L·atm}}{\text{mol·K}})} = 22.9\text{ mol}$$

The molar mass of $C_2H_2F_4$ is 102.03 g/mol, so the mass required for this refrigerant is:

$$22.9\text{ mol}(102.03\text{ g/mol}) = 2340g$$

The molar mass of $C_3H_2F_6$ is 152.04 g/mol, so the mass required for this refrigerant is:

$$22.9\text{ mol}(152.04\text{ g/mol}) = 3480g$$

Green Chemistry Connection

Even though the HFCs used in the worked example have lower ozone depletion potentials than CFCs, they were later found to be potent greenhouse gases. The potency of a greenhouse gas is quantified using Global Warming Potentials (GWPs), a measure of the amount of heat that a compound traps in the Earth's atmosphere per unit mass in relation to carbon dioxide (by definition, GWP for CO_2 equals 1). Compounds with higher GWP values therefore trap more heat in the atmosphere compared to compounds with lower GWP values.

For example, $C_2H_2F_4$ has a GWP of about 1530, meaning that releasing 1 kg of $C_2H_2F_4$ has approximately the same warming effect over 100 years as releasing 1530 kg of carbon dioxide. Similarly, $C_3H_2F_6$ has a GWP of 1340. Notice that the air-conditioning unit in the worked example contains several kilograms of refrigerant. Even a relatively small leak can therefore release a significant amount of a potent greenhouse gas into the atmosphere. This led chemists to develop a new generation of refrigerants with much lower GWPs.

Latest-Generation Refrigerants

Once HFCs were recognized as potent greenhouse gases, chemists began developing a new generation of refrigerants. These compounds, known as hydrofluoroolefins (HFOs), contain a carbon–carbon double bond that allows them to break down rapidly in the atmosphere. As a result, HFOs have negligible ozone depletion potential and very low GWPs.

However, HFOs are not without environmental concerns. Their atmospheric degradation can produce persistent fluorinated compounds, including trifluoroacetic acid (TFA). TFA has been detected throughout the world, including in Antarctica, highlighting the widespread distribution of these degradation products. As a result, the search for refrigerants that are both effective and environmentally sustainable continues.

Using the Ideal Gas Equation to Compare Conditions

When a gas is described under two different sets of conditions, the ideal gas equation can be applied separately to the initial state and the final state:

$$\begin{array}{cc} \text{Initial condition } (i) & \text{Final condition}(f) \\ P_iV_i = n_iRT_i & P_fV_f = n_fRT_f \end{array}$$

Since the gas constant R is the same in both cases, we can rearrange both equations to solve for R:

$$R = \frac{P_iV_i}{n_iT_i} \qquad R = \frac{P_fV_f}{n_fT_f}$$

Because both expressions are equal to the same constant R, we can set them equal to each other:

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f} \tag{4.4.2}$$

This equation, known as the combined gas law, is particularly useful when comparing a gas under two different conditions. If one or more gas properties remain constant between the two states, the equation can be simplified by cancelling out those terms, as seen in the following examples.

Example 4.4.3

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the almost empty aerosol can into a fire at 750 °C. What would be the pressure inside the can (if it did not explode)? The pressure of the can is 1.5 atm at 25 °C.

Given: initial temperature and pressure

Asked for: final pressure

Strategy:

Do you expect the pressure to increase or decrease with an increase in temperature? It is useful to ask yourself this as a check of your final answer.

We can use $\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$. We know that the volume of the can and the amount of gas in the can does not change on heating, therefore $V_i = V_f$ and $n_i = n_f$, so we can cancel those variables.

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$

$$\frac{P_i\cancel{V_i}}{\cancel{n_i}T_i} = \frac{P_f\cancel{V_f}}{\cancel{n_f}T_f}$$

We then have a relationship between the temperature and pressures before and after the can is heated in the fire.

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

In addition, we need to consider the units for temperature. The temperatures need to be converted to K.

Solution:

First convert to K:

25°C + 273 = 298 K

750 °C + 273 = 1023 K

By solving the equation for P_f, we get:

$$\begin{aligned} P_f &= P_i \times \frac{T_f}{T_i} \\ &= 1.5 \text{ atm} \times \frac{1023 \text{ K}}{298 \text{ K}} \\ &= 5.1 \ atm \end{aligned}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

Example 4.4.4: 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 4.4.8). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a temperature of 37 °C at a depth of approximately 20 m where the pressure is 3.13 atm?



Figure 4.4.8: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)
This photograph shows a scuba diver underwater with a tank on his or her back and bubbles ascending from the breathing apparatus.

Let's define the initial conditions as the air in the tank and the final conditions as the air in the lungs:

We can use $\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$. We know that the the moles of air does not change , therefore $n_i = n_f$, so we can cancel those variables.

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$

$$\frac{P_iV_i}{\cancel{n_i}T_i} = \frac{P_fV_f}{\cancel{n_f}T_f}$$

$$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}$$

The temperature must be converted to K.

Solving for V_f:

$$V_f = \frac{(153\ \cancel{\text{atm}})(13.2\ \text{L})(310\ \cancel{\text{K}})}{(300\ \cancel{\text{K}})(3.13\ \cancel{\text{atm}})} = 667\ \text{L}$$

(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.)

Exercise 4.4.2

A helium-filled balloon with a volume of 2.00 L at 22°C is placed into a large container of liquid nitrogen (T = –196°C). What is the final volume of the gas in the balloon?

Answer available at the end of this section.

Exercise 4.4.3

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21 °C at the factory, is accidentally left in the sun in a closed car in Toronto in July. The interior temperature of the car rises to 71 °C. What is the internal pressure in the fire extinguisher?

Answer available at the end of this section.

Exercise 4.4.4

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.

Answer available at the end of this section.

Standard Conditions of Temperature and Pressure

The volume of a gas changes with variations in pressure and temperature. To make comparisons easier, chemists use standard temperature and pressure (STP), which is defined as 273.15 K (0.00°C) and 1 atm. Under these conditions, one mole of an ideal gas occupies approximately 22.4 L, a value known as the standard molar volume.

In many laboratory settings, chemists often work at 1 atm pressure, which was used in an older definition of STP. Under this older convention, one mole of an ideal gas occupies about 22.4 L.

Another commonly used reference condition is standard ambient temperature, set at 25°C (298.15 K). Regardless of the specific gas, any ideal gas at the same temperature and pressure will occupy the same volume, as illustrated in Figure 4.4.9.

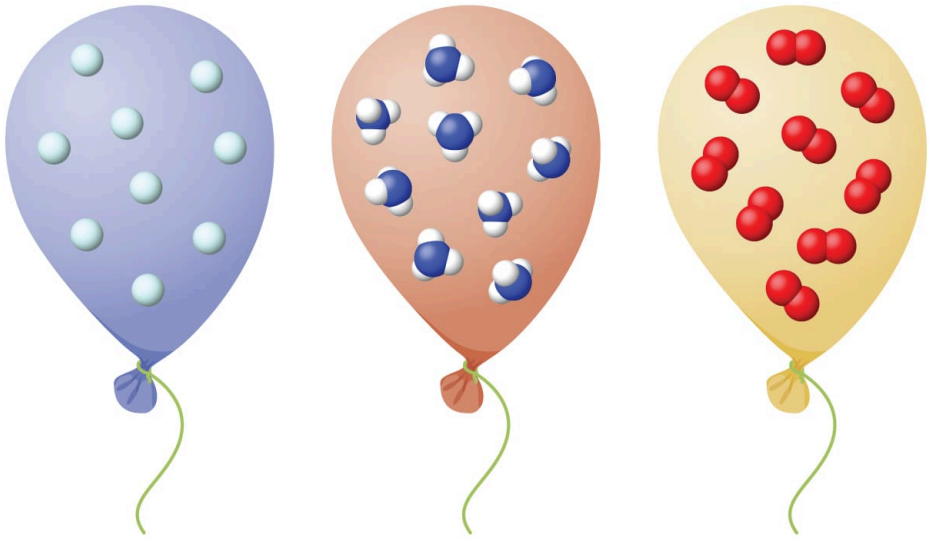


Figure 4.4.9: Each of these balloons contains one mole of a different ideal gas at the same conditions of temperature and pressure, so the balloons have the same volume.

Summary

The properties of gases, pressure (P), volume (V), temperature (T), and moles (n), are interrelated through several experimentally observed gas laws. At constant volume, pressure is directly proportional to temperature. At constant pressure, volume is directly proportional to temperature. At constant temperature, pressure and volume are inversely proportional. At constant temperature and pressure, volume is directly proportional to the number of moles of gas. These relationships can be combined into the ideal gas law, $PV = nRT$, which describes the behaviour of gases under many conditions. Most gases behave ideally under typical pressure and temperature conditions. The ideal gas law can also be used to compare a gas under different sets of conditions. Under standard temperature and pressure (0.00°C, 1 atm), one mole of an ideal gas occupies approximately 22.4 L.

Glossary

absolute zero
: 0 K or –273 °C; the lowest possible temperature.

ideal gas
: A hypothetical gas that behaves exactly as predicted by the ideal gas law.

ideal gas law
: Describes the behaviour of gases under many conditions; $PV = nRT$.

standard molar volume
: The volume one mole of an ideal gas occupies at STP, defined as 22.4 L.

standard temperature and pressure (STP)
: 273.15 K (0.00°C) and 1 atm; universal standard conditions used to compare gas properties.

Answers

Exercise 4.4.1

$$P = \frac{nRT}{V} = \frac{(2520\text{mol})\left(0.08206\ L\ \text{atm mol}^{-1}\text{K}^{-1}\right)\left(3.00 \times 10^2\ \text{K}\right)}{180.0\ \text{L}} = 345\ \text{atm}$$

Exercise 4.4.2

Note: in this case pressure and moles are constant, so:

$$\frac{\cancel{P_i}V_i}{\cancel{n_i}T_i} = \frac{\cancel{P_f}V_f}{\cancel{n_f}T_f}$$

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

T_i = 22°C + 273 = 295 K

T_f = −196°C + 273 = 77 K

$$\frac{2.00L}{295K} = \frac{V_f}{77K}$$

V_f = 0.52 L

Exercise 4.4.3

$$\begin{aligned} P_f &= P_i \times \frac{T_f}{T_i} \\ &= 20.0 \text{ atm} \times \frac{344 \text{ K}}{294 \text{ K}} \\ &= 23.4 \ atm \end{aligned}$$

Exercise 4.4.4

0.193 L

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4.5: Further Applications of the Ideal-Gas Equation

Learning Objectives

- Apply the ideal gas equation to find the density and molar mass of gases.
- Apply the ideal gas equation and the stoichiometry of a reaction to find the amount gas produced or consumed in a reaction.

The ideal gas equation relates pressure, volume, temperature, and the number of moles of a gas. In this section, we will explore how this equation can be applied to determine gas density and molar mass and calculate reactant and product quantities in chemical reactions involving gases. While no new concepts are introduced here, these applications demonstrate how the gas laws integrate into broader chemical calculations.

Gas Densities and Molar Mass

The ideal-gas equation can be rearranged to solve various problems, including the density and molar masses of gases.

Determining Gas Density

The density of a substance, represented by the Greek letter ρ, is the ratio of its mass to its volume:

$$\rho = \frac{m}{V}$$

This definition applies to solids, liquids, and gases. To find the density of a gas, we can use the ideal gas law:

$$PV = nRT$$

Rearranging this equation gives the ratio of moles to volume for a gas:

$$\frac{n}{V} = \frac{P}{RT} \tag{4.5.1}$$

To calculate gas density, we need this ratio in terms of mass, rather than moles. The molar mass (M) relates the mass and number of moles :

$$\mathscr{M} = \frac{m}{n}$$

Rearranging gives:

$$m = \mathscr{M}n$$

Multiplying equation 4.5.1 by the molar mass gives:

$$\mathscr{M}\left(\frac{n}{V}\right) = \mathscr{M}\left(\frac{P}{RT}\right)$$
$$\frac{m}{V} = \frac{\mathscr{M}P}{RT}$$
$$\rho = \frac{\mathscr{M}P}{RT}$$

This equation lets us calculate the density of a gas if we know its molar mass, pressure, and temperature. It also shows how gas density increases with pressure and decreases with temperature, consistent with the behaviour of gases.

Example 4.5.1

What is the density of nitrogen gas (N_2) at 248.0 Torr and 18° C?

Solution

Given:

- P = 248.0 Torr
- V = ?
- n = ?
- R = 0.08206 L atm (mol^{-1})(K^{-1})
- T = 18 °C

Convert units:

$$(248\ \text{Torr}) \times \frac{1\ \text{atm}}{760\ \text{Torr}} = 0.3263\ \text{atm}$$

$$18\,^oC + 273 = 291K$$

Manipulate the ideal gas equation:

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} = \frac{0.3263atm}{(0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}})(291K)} = 0.0137mol/L$$

To get density, we need mass/volume (g/L), not moles/L, so we need to multiply by the molar mass of N_2, 28.02 g/mol:

$$0.0137\frac{\cancel{mol}}{L} \times 28.02\frac{g}{\cancel{mol}}$$

=0.383g/L

Determining Molar Mass

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*:

$$\mathscr{M} = \frac{\text{grams of substance}}{\text{moles of substance}} = \frac{m}{n}$$

$$n = \frac{PV}{RT}$$

Combining these equations, so we can write an equation for molar mass of a gas.:

$$\mathscr{M} = \frac{mRT}{PV}$$

Instead of memorizing separate equations for density and molar mass, you can derive them from the ideal gas equation when needed. This approach simplifies problem-solving and reinforces the relationships between gas properties.

Exercise 4.5.1

A gas that weighs 3.243×10^{-2} g exerts a pressure of 0.315 atm in a 56.0-mL bulb at 55.0 °C. What is the molar mass of the gas?

Answer available at the end of this section.

Stoichiometry and Gases

Stoichiometry describes the quantitative relationships between reactants and products in a chemical reaction. To relate the consumption of reactants with the production of products, you need to use moles. Mass and molecular weight are commonly used to determine the number of moles of a solid. Solution volume and molarity can be used for solutions. The ideal gas equation allows us to determine the number of moles of a gas when its pressure, volume, and temperature are known.

Since all ideal gases contain the same number of molecules in the same volume at a given temperature and pressure, the ratios of gas volumes in a reaction match the stoichiometric coefficients in the balanced chemical equation.

For example, in the reaction between nitrogen and hydrogen to form ammonia:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$$

At constant temperature and pressure:

- 1 volume of $\mathrm{N_2}$ reacts with 3 volumes of $\mathrm{H_2}$
- 2 volumes of $\mathrm{NH_3}$ are produced

This occurs because equal volumes of gases at the same conditions contain equal numbers of molecules (Figure 4.5.1).

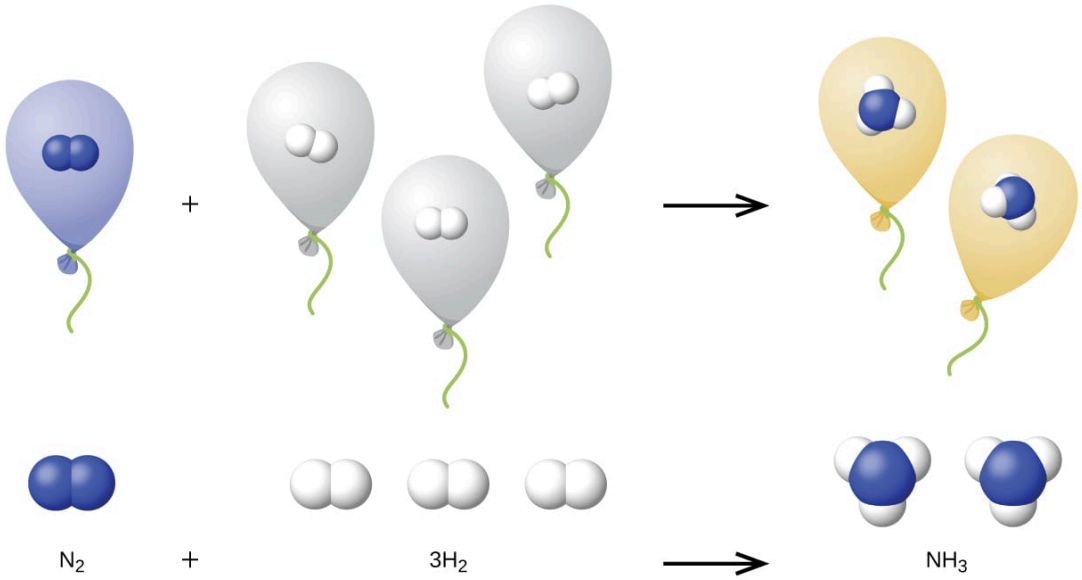


Figure 4.5.1: *One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.* Equal volumes of gaseous $\mathrm{N_2}$, $\mathrm{H_2}$, and $\mathrm{NH_3}$, at the same temperature and pressure, contain the same number of molecules. Because one molecule of $\mathrm{N_2}$ reacts with three molecules of $\mathrm{H_2}$ to produce two molecules of $\mathrm{NH_3}$, the volume of $\mathrm{H_2}$ required is three times the volume of $\mathrm{N_2}$, and the volume of $\mathrm{NH_3}$ produced is two times the volume of $\mathrm{N_2}$.

Example 4.5.2: Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.8 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

Start with a balanced equation for the reaction:

$$C_3H_8(g)+5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

There are two ways to approach this problem.

Method 1: We can determine the moles of C_3H_8 present from the ideal gas law. We can then use the coefficients in the balanced reaction to determine the moles of O_2 needed and then the ideal gas law to find the volume.

$$n_{propane} = \frac{PV}{RT}$$

$$n_{propane} = \frac{(1.00atm)(2.8L)}{(0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}})(298K)} = 0.115mol$$

For each mol of C_3H_8, 5 mol of O_2 react:

$$0.115\ \cancel{\text{mol } C_3H_8}\left(\frac{5\text{ mol } O_2}{1\ \cancel{\text{mol } C_3H_8}}\right) = 0.57\text{ mol } O_2$$

Then we can calculate the volume using the ideal gas equation:

$$V = \frac{nRT}{P}$$

$$V = \frac{(0.57mol)(0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}})(298K)}{1.00atm} = 14L$$

Method 2:

$$C_3H_8(g)+5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$
$$1\text{ volume} + 5\text{ volumes} \longrightarrow 3\text{ volumes} + 4\text{ volumes}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.8\ \cancel{\text{L } C_3H_8} \times \frac{5\text{ L } O_2}{1\ \cancel{\text{L } C_3H_8}} = 14\text{ L } O_2$$

A volume of 14 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 4.5.2

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O$$

Since temperature and pressure are constant, we can work in volume for the stoichiometry of the reaction:

$$2\,C_2H_2(g)+5\,O_2(g) \longrightarrow 4\,CO_2(g)+2\,H_2O(l)$$
$$2 \text{ volume} + 5 \text{ volumes} \longrightarrow 4 \text{ volumes} + 2 \text{ volumes}$$

From the equation, we see that two volumes of C_2H_2 will react with five volumes of O_2:

$$9340\text{ L } C_2H_2\left(\frac{5\,O_2}{2\,C_2H_2}\right) = 23350\text{ L } O_2$$

Answer available at the end of this section.

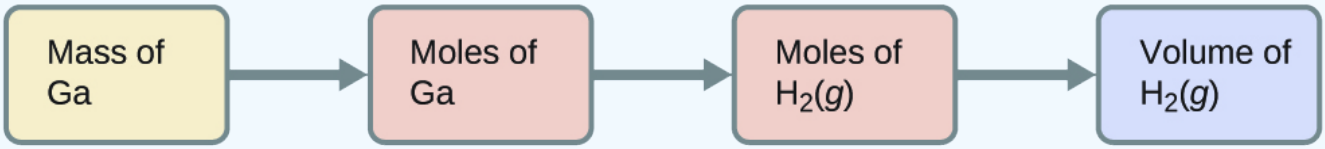
Example 4.5.3: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 mmHg may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$2\,Ga(s) + 6\,HCl(aq) \longrightarrow 2\,GaCl_3(aq) + 3\,H_2(g)$$

Solution

Here is a map of the steps involved:



The first two steps are done here:

$$8.88\,\cancel{\text{g Ga}} \times \frac{1\,\cancel{\text{mol Ga}}}{69.723\,\cancel{\text{g Ga}}} \times \frac{3\text{ mol } H_2}{2\,\cancel{\text{mol Ga}}} = 0.191\text{ mol } H_2$$

Finally, we can use the ideal gas law:

$$V_{H_2} = \frac{nRT}{P} = \frac{0.191\,\cancel{\text{mol}} \times 0.08206\text{ L }\cancel{\text{atm mol}^{-1}\text{ K}^{-1}} \times 300\,\cancel{\text{K}}}{0.951\,\cancel{\text{atm}}} = 4.94\text{ L}$$

Exercise 4.5.3

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning 1.00 kg of sulfur in oxygen?

$$S(s)+O_2(g) \longrightarrow SO_2(g)$$

Answer available at the end of this section.

Example 4.5.4: Emergency Air bags

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2\,NaN_3 \rightarrow 2\,Na\,(s) + 3\,N_2\,(g)$$

This reaction is used to inflate the air bags in cars that cushion passengers during collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. What volume of $\mathrm{N_2}$ gas forms from the decomposition of a 5.00 g sample of $\mathrm{NaN_3}$ at 21°C and 762 mmHg?

Given: reaction, mass of compound, temperature, and pressure

Asked for: volume of nitrogen gas produced

Strategy:

A. Use the stoichiometry of the reaction to find the moles of $\mathrm{N_2}$ gas produced.

B. Use the ideal gas law to find the volume of gas produced.

Solution:

A. Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of $\mathrm{N_2}$ gas produced:

$$\frac{5.00\text{ g NaN}_3}{(22.99+3\times14.01)\text{ g/mol}}\times\frac{3\text{mol N}_2}{2\text{mol NaN}_3}=0.115\text{ mol N}_2$$

B. Solving the ideal gas law for *V* and substituting the other quantities (in the appropriate units), we get

$$V=\frac{nRT}{P}=\frac{0.115\text{ mol}\times0.08206\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}\times294\text{ K}}{1.00\text{ atm}}=2.77\text{ L}$$

Summary

The ideal gas law can be used to determine the density and molar mass of gases.

The stoichiometric relationships between reactants and products can be expressed in terms of moles, masses, solution volumes, or gas volumes. The ideal gas law allows us to calculate the quantities of gaseous reactants and products involved in a chemical reaction.

Answers

Exercise 4.5.1

We know the mass of the gas sample, so if we find the moles of gas we can determine the molar mass:

$$n=\frac{PV}{RT}=\frac{(0.315atm)(0.0560L)}{(0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}})(823K)}=2.61\times10^{-4}$$

$$\frac{3.243\times10^{-2}g}{2.61\times10^{-4}mol}=124g/mol$$

Exercise 4.5.2

Each tank contains 7.00×10^3 L of $\mathrm{O_2}$.

Find the number of tanks:

$$23350\text{ L}\left(\frac{\text{tank}}{7.00\times10^3\text{ L}}\right)=3.34\text{ tanks}$$

Exercise 4.5.3

1.30×10^3 L

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4.6: Gas Mixtures and Partial Pressures

Learning Objectives

- Determine the contribution of each component gas to the total pressure of a mixture of gases
- Relate the mole fraction and partial pressures of gases to the total pressure and composition of a gas mixture

So far, we have used the ideal gas law to describe pure gases—those made of only one chemical species. But what happens when we mix two or more gases? In this section, we will explore how to determine the contribution of each gas to the total pressure of a mixture.

Partial Pressures

The ideal gas law assumes that all gases behave the same way, regardless of their chemical identity. It also assumes that gas particles do not attract or repel each other. If the volume and temperature remain constant, we can rearrange the ideal gas equation to show that the pressure of a gas depends only on the number of moles present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{constant}$$

Note that nothing in the equation depends on the identity of the gas; only the amount of gas affects the pressure.

Consider a mixture of two ideal gases in equal amounts. What will the total pressure be? Since pressure depends only on the total number of gas particles, the total pressure of the mixture will be twice the pressure of either gas alone. More generally, the total pressure of a gas mixture is the sum of the pressures that each gas would exert if it were alone in the container.

Each individual gas in a mixture has its own contribution to the total pressure, called its partial pressure. The sum of these partial pressures gives the total pressure of the gas mixture. This principle, discovered by John Dalton, is known as Dalton's Law of Partial Pressures:

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots \tag{4.6.1}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases. Figure $4.6.1$ shows three gases, He, $\mathrm{N_2}$, and $\mathrm{O_2}$, in separate containers. If these gases are added to one container of the same volume at a constant temperature, the total pressure is the sum of the partial pressures of the three gases.

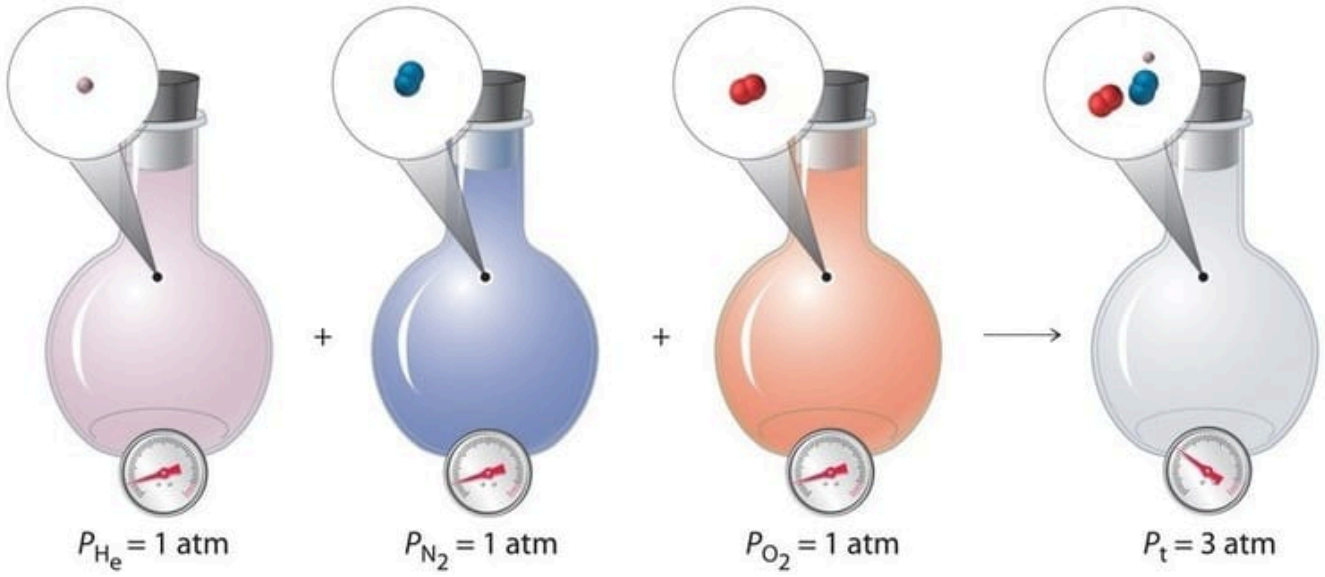


Figure 4.6.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$\begin{aligned} P_{tot} &= P_A + P_B \\ &= n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) \\ &= (n_A + n_B)\left(\frac{RT}{V}\right) \end{aligned}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (n_1 + n_2 + n_3 + \cdots + n_n)\left(\frac{RT}{V}\right) \tag{4.6.2}$$

This equation confirms that, at constant temperature and volume, the total pressure of a gas depends only on the total number of moles present, not on the type of gas. This holds as long as the gas behaves ideally—that is, the particles do not interact with each other and their individual properties do not affect the overall pressure.

The calculation of total and partial pressures for mixtures of gases is illustrated in Example 4.6.1.

Example 4.6.1: The Bends

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 100 m, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of gases, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of He and O_2 present.
B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A. The number of moles of He is

$$n_{\mathrm{He}} = \frac{326.4\ \mathrm{g}}{4.003\ \mathrm{g/mol}} = 81.54\ \mathrm{mol}$$

The number of moles of $\mathrm{O_2}$ is

$$n_{\mathrm{O_2}} = \frac{51.2\ \mathrm{g}}{32.00\ \mathrm{g/mol}} = 1.60\ \mathrm{mol}$$

B. We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\mathrm{He}} = \frac{n_{\mathrm{He}}RT}{V} = \frac{81.54\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 196\ \mathrm{atm}$$

$$P_{\mathrm{O_2}} = \frac{n_{\mathrm{O_2}}RT}{V} = \frac{1.60\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 3.85\ \mathrm{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\mathrm{tot}} = P_{\mathrm{He}} + P_{\mathrm{O_2}} = (196 + 3.85)\ \mathrm{atm} = 200\ \mathrm{atm}$$

Exercise 4.6.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane, $\mathrm{CH_4}$, and 336 g of ethane, $\mathrm{C_2H_6}$. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer available at the end of this section.

Mole Fractions of Gas Mixtures

A gas mixture can be described by the mole fractions of the gases present. The mole fraction (χ) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles present in the mixture (n_{tot}):

$$\chi_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{4.6.3}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $\chi_A = 1.0$, then the sample is entirely composed of A, meaning no other gases are present. If $\chi_A = 0$, then no A is in the mixture. The sum of the mole fractions of all the components in a mixture must always equal 1.

To see how mole fractions help describe gas mixtures, let's compare the pressure of a gas to the total pressure of the mixture. Using the ideal gas law:

$$P_A = n_A RT/V \text{ and } P_{tot} = n_{tot}RT/V$$

Taking the ratio of these pressures:

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot}RT/V} = \frac{n_A}{n_{tot}} = \chi_A$$

Rearranging this gives:

$$P_A = \chi_A P_{tot} \tag{4.6.4}$$

This equation shows that the partial pressure of any gas in a mixture equals the total pressure multiplied by the mole fraction of that gas. This result follows directly from the ideal gas law, which assumes all gas particles behave ideally.

For example, Earth's atmosphere is approximately 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of other gases such as CO_2, H_2O and others. This means that 78% of the particles present in the atmosphere are N_2; the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Assuming an atmospheric pressure of 1.00 atm, we can calculate their partial pressures:

- $P_{N_2} = \chi_{N_2} P_{tot} = 0.78(1.00) = 0.78 atm$
- $P_{O_2} = \chi_{O_2} P_{tot} = 0.21(1.00) = 0.21 atm$
- $P_{Ar} = \chi_{Ar} P_{tot} = 0.009(1.00) = 0.009 atm$

These calculations illustrate how mole fractions help determine partial pressures in real-world gas mixtures.

Example 4.6.2: Exhaling Composition

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

	Inhaled Air / mmHg	Exhaled Air / mmHg
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 4.6.4.

Solution:

The mole fraction of any gas A is given by

$$\chi_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$\chi_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of χ_A for the gases in the exhaled air.

Gas	Mole Fraction
N_2	0.741

Gas	Mole Fraction
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

Exercise 4.6.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer available at the end of this section.

Example 4.6.3

Ammonium nitrate decomposes completely when heated, producing only gaseous products:

$$2\,NH_4NO_3\,(s) \rightarrow 2\,N_2\,(g) + 4\,H_2O\,(g) + O_2\,(g)$$

a) What is the mole fraction of $H_2O\,(g)$ in the product mixture?

b) Ammonium nitrate is decomposed in an evacuated, sealed container. If the partial pressure of $H_2O\,(g)$ is 2.35 atm, what is the total pressure? What is the partial pressure of $O_2\,(g)$?

Solution

a) Use the stoichiometric coefficients from the balanced equation to determine the mole ratios of the gaseous products. For every 2 moles of NH_4NO_3 that decompose, the reaction produces:

- 2 mol N_2
- 4 mol H_2O
- 1 mol O_2

Total moles of gas = 2 + 4 + 1 = 7 mol

Mole fraction of H_2O:

$$\chi_{H_2O} = \frac{4}{7} = 0.571$$

b) Mole fractions are proportional to partial pressure and the total pressure:

$$P_{H_2O} = \chi_{H_2O} \cdot P_{total}$$

This equation can be rearranged to solve for the total pressure:

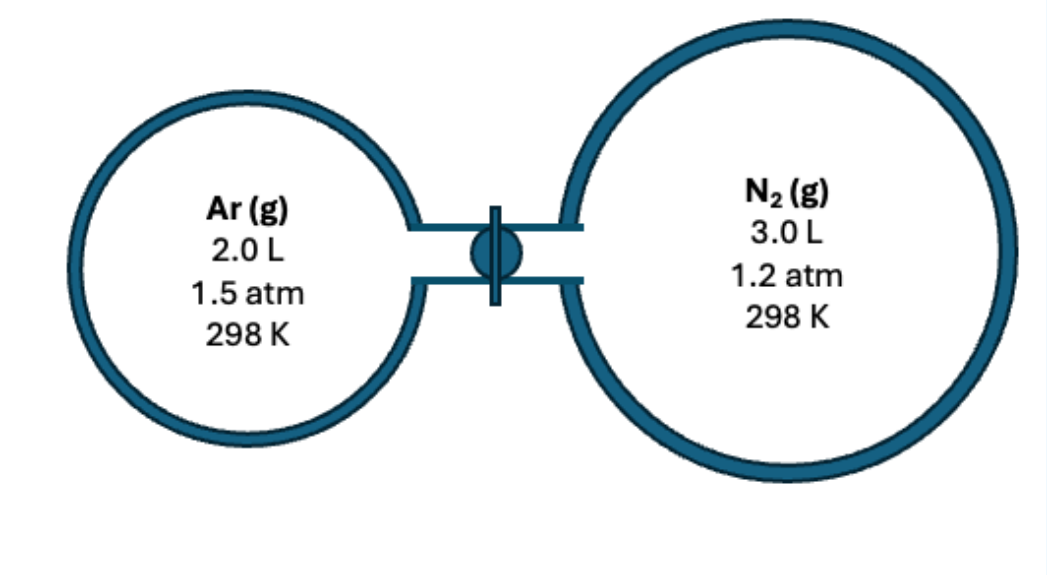
$$P_{total} = \frac{P_{H_2O}}{\chi_{H_2O}} = \frac{2.35\text{ atm}}{4/7} = 2.35 \times \frac{7}{4} = 4.11\text{ atm}$$

We can then use the mole fraction of O_2 to calculate its partial pressure:

$$\chi_{O_2} = \frac{1}{7} \quad \Rightarrow \quad P_{O_2} = \chi_{O_2} \cdot P_{total} = \frac{1}{7} \cdot 4.11 = 0.587\text{ atm}$$

Exercise 4.6.3

Two containers are connected by a valve. When the valve is opened, the gases mix at 298 K/



.

(a) What is the partial pressure of $\mathrm{Ar}(g)$ after mixing?

(b) What is the partial pressure of $\mathrm{N}_2(g)$ after mixing?

(c) What is the total pressure?

Answer available at the end of this section.

Summary

The pressure exerted by an individual gas in a mixture is known as its partial pressure and is directly proportional to its mole fraction. The partial pressure of each gas is independent of the pressures exerted by other gases in the mixture. The total pressure of a gas mixture is the sum of the partial pressures of all its components.

The amount of any gas in a mixture can be described by its partial pressure or its mole fraction. The mole fraction is the ratio of the number of moles of a specific gas to the total number of moles of all gases present. In a gas mixture, the partial pressure of each gas can be calculated by multiplying the total pressure by the mole fraction of that gas.

Glossary

Dalton's law of partial pressures
: States that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the individual gases.

partial pressure
: The pressure exerted by an individual gas in a mixture of gases, independent of the pressures exerted by other gases.

total pressure
: The sum of the pressures that each gas in a mixture would exert if it were alone in the container.

Answers

Exercise 4.6.1

$$1813 \text{ g } \text{CH}_4 \left(\frac{mol}{16.04g}\right) = 113.0mol \; P_{CH_4} = \frac{nRT}{V} = \frac{(113.0mol)(0.08206 \; \frac{atm \cdot L}{mol \cdot K})(295K)}{20.0L} = 137atm$$

$$336 \text{ g } \text{C}_2\text{H}_6 \left(\frac{mol}{30.07g}\right) = 11.2mol \; P_{C_2H_6} = \frac{nRT}{V} = \frac{(11.2mol)(0.08206 \; \frac{atm \cdot L}{mol \cdot K})(295K)}{20.0L} = 13.5atm$$

P_{tot} = 137 atm + 13.5 atm = 151 atm

Exercise 4.6.2

$$P_{\text{CO}_2} = 86 \text{ atm}$$
$$P_{\text{N}_2} = 2.7 \text{ atm}$$

Exercise 4.6.3

(a) We can approach this problem in several ways. Since the moles of $\text{Ar}(g)$ and the temperature are constant, we can cancel those variables. The final volume is 2.0 L + 3.0 L = 5.0 L:

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$
$$\frac{P_iV_i}{\cancel{n_i}\;\cancel{T_i}} = \frac{P_fV_f}{\cancel{n_f}\;\cancel{T_f}}$$
$$P_f = \frac{P_iV_i}{V_f}$$
$$P_f = \frac{(1.5 \text{ atm})(2.0 \text{ L})}{(5.0 \text{ L})} = 0.60 \text{ atm}$$

The partial pressure of Ar is 0.60 atm.

(b)

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$
$$\frac{P_iV_i}{\cancel{n_i}\;\cancel{T_i}} = \frac{P_fV_f}{\cancel{n_f}\;\cancel{T_f}}$$
$$P_f = \frac{P_iV_i}{V_f}$$
$$P_f = \frac{(1.2 \text{ atm})(3.0 \text{ L})}{(5.0 \text{ L})} = 0.72 \text{ atm}$$

The partial pressure of N_2 is 0.72 atm.

(c) The total pressure is the sum of the partial pressures:
0.60 atm + 0.72 atm = 1.32 atm.

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4.7: The Kinetic-Molecular Theory

Learning Objectives

- Use the kinetic molecular theory to describe the properties of gases, such as kinetic energy, speed, and relative rates of effusion and diffusion.
- Use this theory's postulates to explain the gas laws

The gas laws we have discussed so far, including the ideal gas equation, are empirical; they are based on experimental observations. These mathematical laws describe the macroscopic behaviour of most gases at pressures below 1–2 atm. While gas laws describe relationships observed in experiments, they do not explain why gases behave this way. The kinetic molecular theory (KMT) provides a microscopic model to explain these observations.

The usefulness of the kinetic molecular theory (KMT) lies in its ability to explain gas behavior. The assumptions of KMT provide a conceptual basis for understanding the gas laws, supporting the idea that these assumptions reasonably describe gas particles. We will first examine the individual gas laws to see how KMT accounts for their relationships. Then, we will explore how particle mass, speed, and kinetic energy relate to temperature in more detail.

The kinetic molecular theory (KMT) is a simple microscopic model that provides a conceptual explanation for the gas laws. This theory is based on five key postulates:

- Gas particles move continuously in straight lines, changing direction only upon collisions.
- The size of gas particles is negligible compared to the space between them.
- Gas pressure results from collisions between particles and the container walls.
- Gas particles do not attract or repel each other; all collisions are elastic (no energy loss).
- The average kinetic energy of gas particles is directly proportional to temperature in Kelvin.

(Note: The term "particle" refers to individual gas species, whether atomic or molecular.)

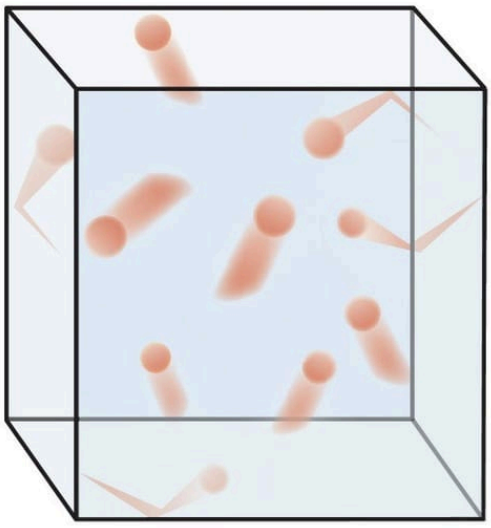


Figure 4.7.1: Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

The Kinetic-Molecular Theory and Gas Laws

Gas pressure results from collisions of rapidly moving gas particles with the walls of the container. The frequency and force of these collisions depend directly on the number of particles striking a given area per unit of time. Using this idea, we can see how

the kinetic molecular theory (KMT) conceptually explains gas behaviour:

- **Temperature and Pressure:** When temperature increases, the average speed and kinetic energy of gas particles increase. If volume is held constant, the faster particles collide with the container walls more frequently and with greater force, increasing the pressure. (Figure $4.7.2a$).
- **Temperature and Volume:** Increasing temperature increases the kinetic energy of gas particles, making them move faster. To maintain constant pressure, the volume must increase. As the volume expands, gas particles travel longer distances between collisions, and the container's surface area increases. This reduces both the collision frequency with the walls and the number of collisions per unit area, counteracting the increased collision force due to higher kinetic energy.
- **Pressure and Volume:** When gas volume decreases, particles travel shorter distances between collisions, and the container's surface area is reduced. These factors lead to more frequent collisions per unit area, increasing pressure (Figure $4.7.2b$).
- **Moles of Gas and Volume:** At constant pressure and temperature, the force and frequency of particle collisions with the walls remain the same. Increasing the number of gas particles requires a proportional increase in volume to maintain a constant collision rate per unit area so that pressure remains unchanged (Figure $4.7.2c$).
- **Partial Pressures and Total Pressure:** In a gas mixture, the particles of each gas move independently in the available space. Since the presence of one gas does not affect the frequency of another gas's collisions with the walls, the total pressure of a mixture equals the sum of the partial pressures of the individual gases.

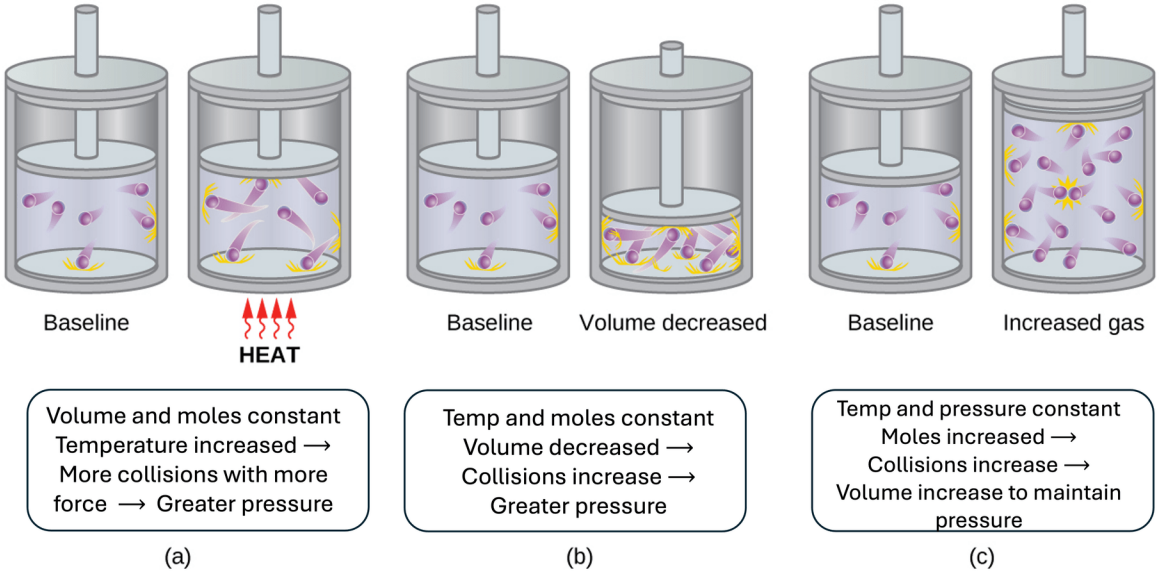


Figure $4.7.2$: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

Molecular Velocities and Kinetic Energy

The postulates of the kinetic molecular theory (KMT) help us understand the relationship between temperature, particle motion, and energy. To explore this, we examine how particle velocities and kinetic energy vary within a gas sample and how these properties depend on temperature and molecular mass.

In a gas sample, individual particles move at widely varying speeds. However, because of the vast number of particles and frequent collisions, the overall distribution of speeds remains constant. This distribution, known as the Maxwell-Boltzmann distribution, represents the relative number of particles in a gas sample that move at a given speed (Figure $4.7.3$).

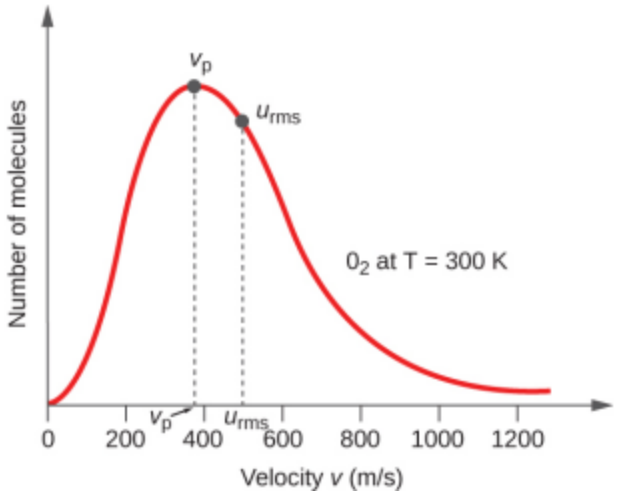


Figure 4.7.3: The molecular speed distribution for oxygen gas at 300 K shows that very few particles move at extremely low or high speeds. The number of particles with intermediate speeds increases rapidly up to a peak, known as the most probable speed (v_p), before decreasing again. The root mean square speed (u_{rms}) is slightly higher than v_p, closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

$$\mathrm{KE} = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m^2 s^{-2}). Since a gas contains a large number of particles, we use averages for both speed and kinetic energy. The root mean square velocity of a particle, u_{rms}, is defined as the square root of the average of the squared velocities, where n is the number of particles:

$$u_{\mathrm{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

The average kinetic energy, KE_{avg}, is then equal to:

$$\mathrm{KE}_{\mathrm{avg}} = \frac{1}{2}mu_{\mathrm{rms}}^2$$

For a mole of gas particles, the KE_{avg} is directly proportional to the Kelvin temperature (T) through this relationship:

$$\mathrm{KE}_{\mathrm{avg}} = \frac{3}{2}RT$$

where R is the gas constant and T is the Kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J $mol^{-1}K^{-1}$ (8.314 kg $m^2s^{-2}mol^{-1}K^{-1}$), which is always what we use when dealing with energy in joules. To find the average kinetic energy per gas molecule, we divide by Avogadro's number (N_A = 6.022 x 10^{-23} particles/mol):

$$\mathrm{KE}_{\mathrm{avg}} = \frac{3}{2}\frac{R}{N_A}T$$

We can combine these equations to express u_{rms} in terms of temperature:

$$\frac{1}{2}mu_{\mathrm{rms}}^2 = \frac{3}{2}\frac{R}{N_A}T$$

Rearranging for u_{rms} gives :

$$u_{\mathrm{rms}} = \sqrt{\frac{3RT}{\mathscr{M}}} \tag{4.7.1}$$

where M is the molar mass (N_A x m). Because we need u_{rms} in m/s and R is in kg $m^2s^{-2}mol^{-1}K^{-1}$, we must convert molar mass from g/mol to kg/mol when doing this calculation. Be careful of unit conversions!

Example 4.7.1: Calculation of u_{rms}

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30°C + 273 = 303\ K$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathscr{M}}}$$

$$u_{\text{rms}} = \sqrt{\frac{3(8.314\frac{\cancel{kg}\,m^2}{\cancel{mol}\,s^2\,\cancel{K}})(303\,\cancel{K})}{28.02\frac{\cancel{g}}{\cancel{mol}}}\left(\frac{1000\,\cancel{g}}{\cancel{kg}}\right)} = 519 m/s$$

Exercise 4.7.1

Calculate the root-mean-square velocity for an oxygen molecule at –23 °C.

Answer available at the end of this section.

When the temperature of a gas increases, its average kinetic energy (KE_{avg}) also increases. This means more particles move at higher speeds, while fewer move at lower speeds. As a result, the speed distribution shifts to the right, towards higher speeds overall. Conversely, when temperature decreases, KE_{avg} decreases, leading to more particles moving at lower speeds and fewer at higher speeds, causing the distribution to shift to the left. This behaviour is illustrated for nitrogen gas in Figure 4.7.4.

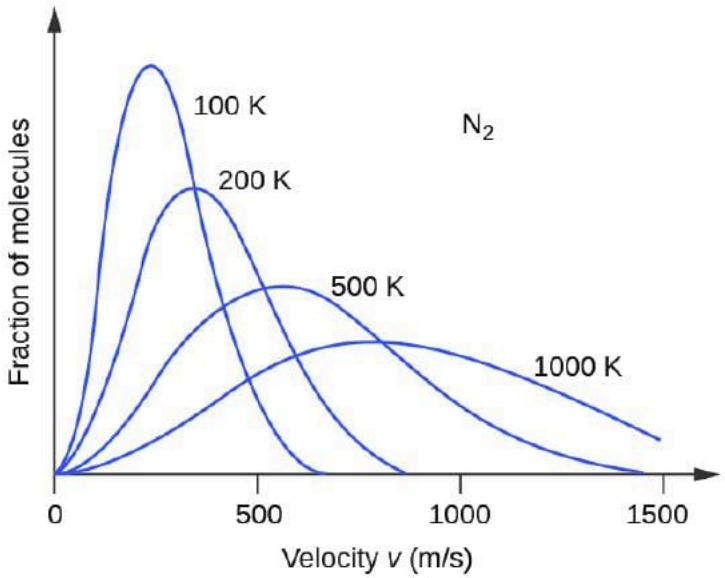


Figure 4.7.4: The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg}, regardless of their identity. However, lighter gas particles move faster on average, while heavier gas particles move slower. Gases with lighter particles have more high-speed particles and a higher root mean square speed (u_{rms}), with a distribution that peaks at higher velocities. In contrast, gases with heavier particles have more slow-moving particles, a lower u_{rms}, and a speed distribution that peaks at lower velocities. This trend is demonstrated by the data for a series of noble gases shown in Figure 4.7.5.

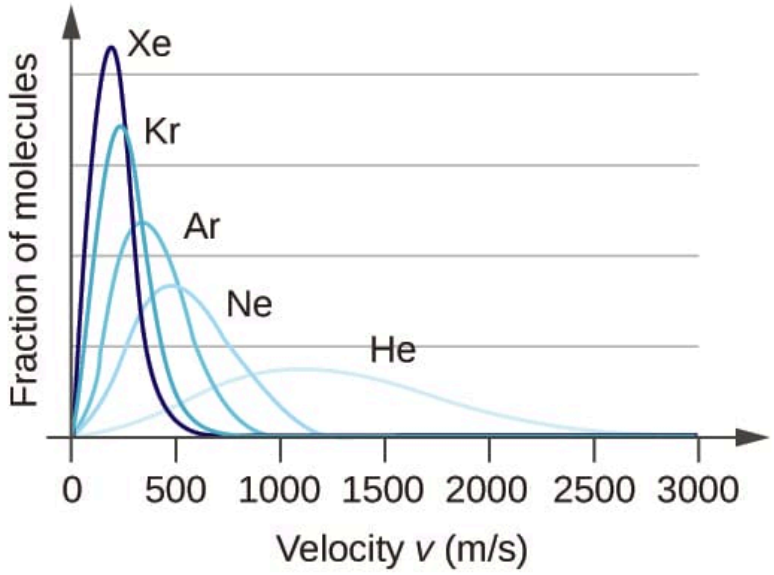


Figure 4.7.5: Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

Example 4.7.2

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on

a. the average kinetic energy of the N_2 molecules?
b. the rms speed of the N_2 molecules?
c. the impact of each N_2 molecule on the wall of the container during a collision with the wall?
d. the total number of collisions per second of N_2 molecules with the walls of the entire container?
e. the pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
b. An increase in average kinetic energy is due to an increase in the rms speed of the gas particles.
c. If, on average, the particles are moving faster, then they strike the container walls with more energy.
d. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
e. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law. This is due to the increased force and number of collisions.

Exercise 4.7.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at a constant temperature. What is the qualitative effect of this change on

a. the average kinetic energy of the He atoms?
b. the rms speed of the He atoms?
c. the impact of each He atom on the wall of the container during a collision with the wall?
d. the total number of collisions per second of He atoms with the walls of the entire container?
e. the pressure of the He gas?

Answer a available at the end of this section.

Effusion and Diffusion

If someone opens a bottle of perfume in the next room, you'll likely smell it soon. This happens because tiny aromatic particles travel through the air to reach your olfactory receptors. But how do these particles move, even without air currents carrying them?

Diffusion is the movement of gas particles from an area of higher concentration to an area of lower concentration, leading to the gradual mixing of gases. This occurs due to the random motion of particles, even without external forces like stirring.

Effusion is a related process but occurs when gas particles pass through a tiny hole into an evacuated space.

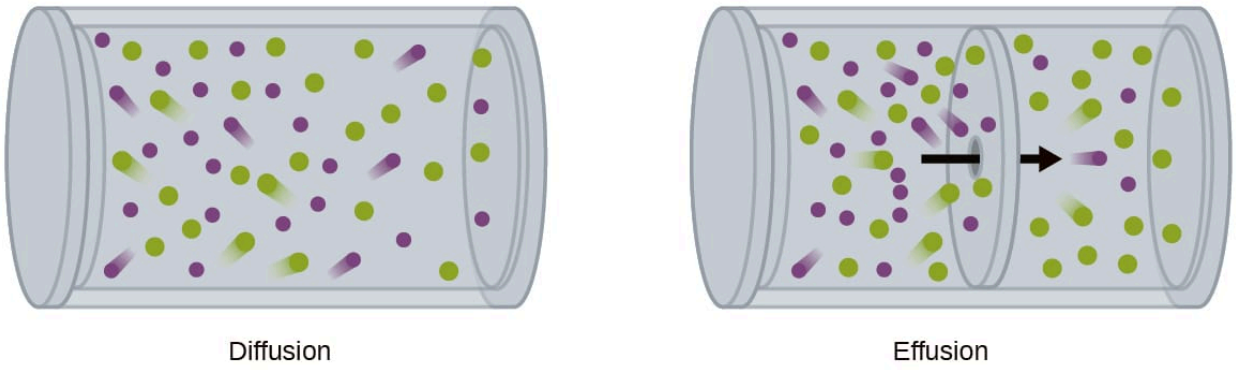


Figure 4.7.6: Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance travelled between collisions. Effectively, this means that only one particle passes through at a time.

$$\text{effusion rate} \propto u_{\text{rms}} \tag{4.7.2}$$

The rates of both diffusion and effusion depend on how fast gas particles move. Faster-moving particles diffuse and effuse more quickly:

$$\text{effusion rate} \propto u_{\text{rms}}$$

$$\text{diffusion rate} \propto u_{\text{rms}}$$

Since lighter gases move faster than heavier gases, they effuse and diffuse more quickly. This effect can be observed in Figure 4.7.7, which shows the diffusion of $\mathrm{H_2}$ and $\mathrm{O_2}$ gases. Because $\mathrm{H_2}$ is much lighter than $\mathrm{O_2}$, its particles move faster and diffuse more rapidly.

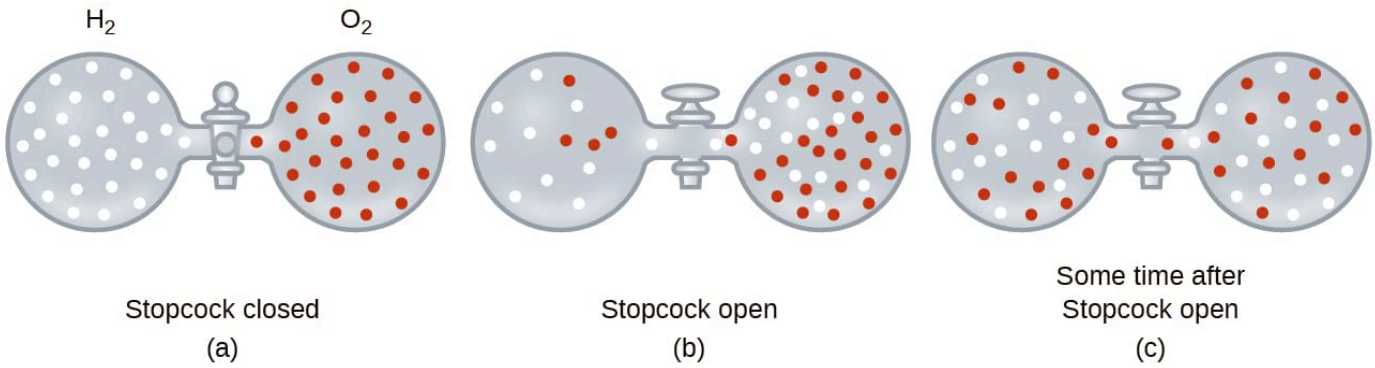


Figure 4.7.7: (a) Two gases, $\mathrm{H_2}$ and $\mathrm{O_2}$, are initially separated. (b) When the stopcock is opened, they begin to mix. The lighter $\mathrm{H_2}$ particles move through the opening more quickly than the heavier $\mathrm{O_2}$ particles. (c) Over time, both gases distribute evenly throughout the vessel.

Summary

The kinetic molecular theory (KMT) is a simple yet effective model that explains ideal gas behaviour. It assumes that gases consist of widely separated particles with negligible volume, moving constantly and colliding elastically with each other and the container walls. The average kinetic energy of gas particles is determined by temperature, but individual particles have a range of kinetic energies at any given temperature.

Gas particles also exhibit a range of velocities, with their speed distribution depending on both temperature and particle mass. The rates of effusion and diffusion are directly proportional to the root mean square (rms) velocity of the gas.

Glossary

average kinetic energy (KE_{avg})
: The mean kinetic energy of particles in a gas; directly proportional to temperature.

diffusion
: The movement of gas particles from an area of higher concentration to an area of lower concentration.

effusion
: The movement of gas particles through an opening smaller than the mean free path of the particles into an evacuated space.

joule (J)
: The SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second; 1 J = 1 kg m^2/s and 4.184 J = 1 cal.

kinetic molecular theory
: Microscopic model explaining ideal gas behavior, postulating that gas particles move in straight lines unless interrupted by elastic collisions, particles are of negligible volume, particles' average kinetic energy is proportional to temperature, and gas pressure results from collisions with the container walls.

Maxwell-Boltzmann distribution
: A function demonstrating the relative number of particles in a gas sample that move at a given speed.

mean free path
: The average distance travelled between gas particle collisions.

root mean square velocity (u_{rms})
: The square root of the average of the squared velocities of particles in a gas.

Answers

Exercise 4.7.1

441 m/s

Exercise 4.7.2

no change (there is no change in temperature)
no change (there is no change in temperature)
no change (there is no change in temperature)
decreases (due to increased volume)
decreases (due to fewer collisions)

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4.E: Gases (Exercises)

States of Matter

Exercise $4.E.1$****

For a substance that has gas, liquid, and solid phases, arrange these phases in order of

a) increasing density

b) compressibility

c) molecular motion.

Answer available at the end of this section.

Gas Pressure

Exercise $4.E.2$****

Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?

Answer available at the end of this section.

Exercise $4.E.3$***

Atmospheric pressure in Vancouver, BC was 102.3 kPa. Calculate this barometric pressure in atm and mmHg.

Answer available at the end of this section.

Exercise $4.E.4$***

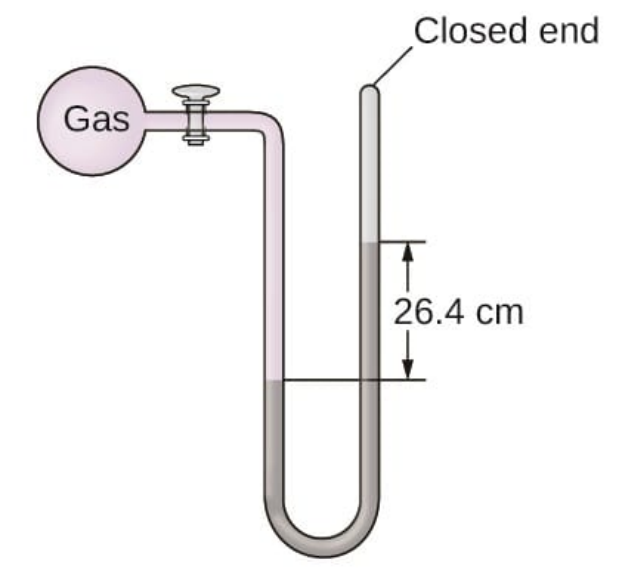
The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. What is this pressure in mmHg?

Answer available at the end of this section.

Exercise $4.E.5$****

The pressure of a sample of gas is measured at sea level with a closed-end manometer as shown in the figure below. The liquid in the manometer is mercury. Determine the pressure of the gas in:

a. mmHg
b. atm

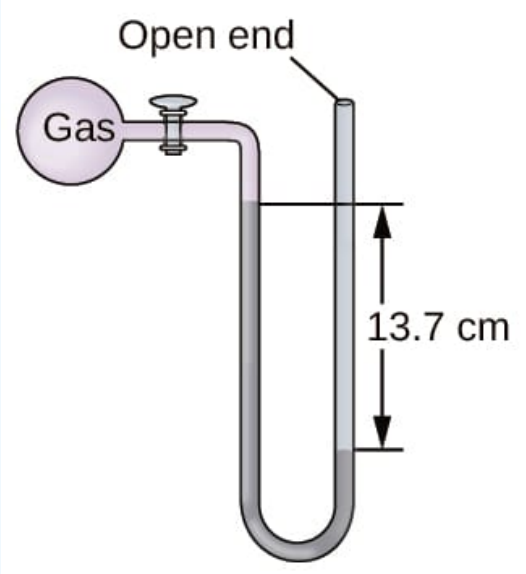


Answer available at the end of this section.

Exercise $4.E.6$**

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760.0 mmHg, determine the pressure of the gas in:

a. mmHg
b. atm



Answer available at the end of this section.

Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

Exercise $4.E.7$*

When a scuba diver exhales gas bubbles, the bubbles rise through the column of water going from higher to lower pressure. Explain how the volume of the bubbles change as they rise to the surface, assuming that they remain intact.

Answer available at the end of this section.

Exercise $4.E.8$*

Calculate the volume of 1.00 mol of $\mathrm{CH_4}$ gas at 150.0 K and 1.00 atm

Answer available at the end of this section.

Exercise $4.E.9$*

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?

Answer available at the end of this section.

Exercise $4.E.10$*

A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

Answer available at the end of this section.

Exercise $4.E.11$**

How many moles of gaseous boron trifluoride, $\mathrm{BF_3}$, are contained in a 4.3410 L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of $\mathrm{BF_3}$?

Answer available at the end of this section.

Exercise $4.E.12$*

A balloon that is 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Blue Mountain in Ontario. If the final volume of the balloon is 144.53 L at a temperature of 5 °C, what is the pressure experienced by the balloon as it clears Blue Mountain?

Answer available at the end of this section.

Exercise $4.E.13$**

Iodine, $\mathrm{I_2}$, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of $\mathrm{I_2}$ vapor at a pressure of 0.462 atm?

Answer available at the end of this section.

Exercise $4.E.14$**

A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

Answer available at the end of this section.

Exercise $4.E.15$**

For a given amount of gas showing ideal behaviour, draw labelled graphs of:

a. the variation of P with V
b. the variation of V with T
c. the variation of P with T
d. the variation of $\frac{1}{P}$ with V

Answer available at the end of this section.

Exercise $4.E.16$*

If the volume of a fixed amount of an ideal gas is tripled at constant temperature, what happens to the pressure?

Answer available at the end of this section.

Exercise $4.E.17$**

Your instructor blows up a balloon so that it is filled with 0.55 moles of helium at 21.5 ^{o}C and 1.00 atm pressure. The instructor adds 0.050 moles of helium to the balloon. If the pressure in the balloon remains the same, do you expect the volume to increase or decrease? Explain your reasoning in clear and complete statements.

Answer available at the end of this section.

Exercise $4.E.18$**

A 8.60 L tank of nitrogen gas at a pressure of 455 mmHg is connected to an empty tank with a volume of 5.35 L. What is the final pressure (in atm) in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.

Answer available at the end of this section.

Exercise $4.E.19$**

The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day?

Answer available at the end of this section.

Applications of the Gas Laws

Exercise $4.E.20$**

Calculate the density of Freon 12, $\mathrm{CF_2Cl_2}$, at 30.0 °C and 0.954 atm.

Answer available at the end of this section.

Exercise $4.E.21$**

What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 Torr?

Answer available at the end of this section.

Exercise $4.E.22$**

What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 Torr?

Answer available at the end of this section.

Exercise $4.E.23$**

The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at 0.00 °C and 1.00 atm. Calculate the molar mass of this gas. Which is the most likely identity of the gas: $\mathrm{PF_3}$, $\mathrm{PF_5}$, or $\mathrm{P_2F_4}$?

Answer available at the end of this section.

Exercise $4.E.24$**

Pure oxygen was first prepared by heating mercuric oxide, HgO:

$$2\,\mathrm{HgO}(s) \longrightarrow 2\,\mathrm{Hg}(l) + \mathrm{O_2}(g)$$

What volume of $\mathrm{O_2}$ at 23 °C and 0.975 atm is produced from the decomposition of 5.36 g of HgO?

Answer available at the end of this section.

Exercise $4.E.25$**

The chlorofluorocarbon $\mathrm{CCl_2F_2}$ can be recycled into a different compound by reaction with hydrogen to produce $\mathrm{CH_2F_2}$, a compound useful in chemical manufacturing:

$$\mathrm{CCl_2F_2}(g) + 4\,\mathrm{H_2}(g) \longrightarrow \mathrm{CH_2F_2}(g) + 2\,\mathrm{HCl}(g)$$

What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton (1.000×10^3 kg) of $\mathrm{CCl_2F_2}$?

Answer available at the end of this section.

Exercise $4.E.26$**

What volume of oxygen is required to react with 12.00 L of ethane gas, $\mathrm{C_2H_6}$, to produce carbon dioxide and water, if the volumes of $\mathrm{C_2H_6}$ and $\mathrm{O_2}$ are measured under the same conditions of temperature and pressure?

$$2\,\mathrm{C_2H_6}(g) + 7\,\mathrm{O_2}(g) \longrightarrow 4\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(g)$$

Answer available at the end of this section.

Gas Mixtures and Partial Pressures

Exercise $4.E.27$**

A 36.0 L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g $\mathrm{CO_2}$, 805 g $\mathrm{O_2}$, and 4880 g $\mathrm{N_2}$. At 25 °C, what is the pressure in the cylinder in atmospheres? What is the mole fraction of $\mathrm{O_2}$ in the mixture? What is the partial pressure of $\mathrm{O_2}$?

Answer available at the end of this section.

Exercise $4.E.28$*

A sample of gas isolated from unrefined petroleum contains 90.0% $\mathrm{CH_4}$, 8.9% $\mathrm{C_2H_6}$, and 1.1% $\mathrm{C_3H_8}$ at a total pressure of 3.03 atm. What is the partial pressure (in atm) of each component of this gas?

Answer available at the end of this section.

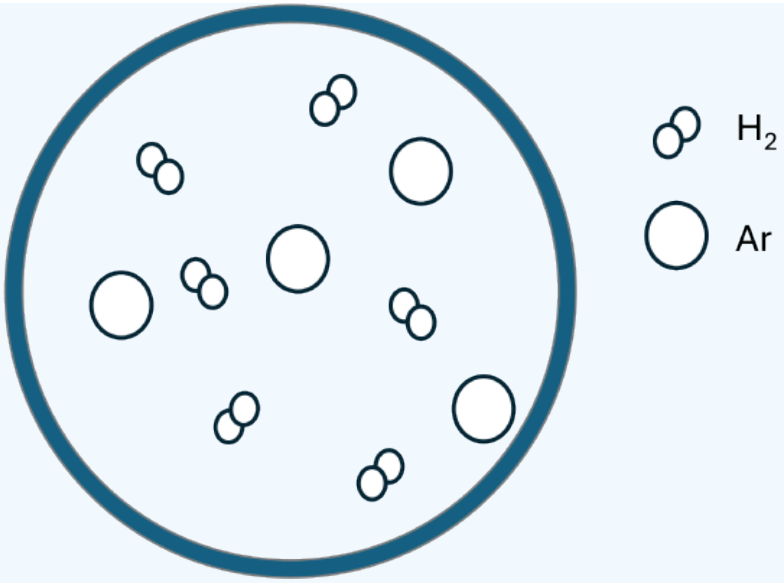
Exercise $4.E.29$**

A 2.00 L container with 2.50 atm of $\mathrm{N_2}$ is connected to a 5.00 L container with 1.90 atm of He. The containers are opened, and the gases mix. What is the final pressure inside the containers? Assume there is no change in temperature.

Answer available at the end of this section.

Exercise $4.E.30$*

Consider the gas mixture of $\mathrm{H_2}$ and Ar shown below:



Which gas has the greater mole fraction? Which gas has the greater partial pressure?

Answer available at the end of this section.

The Kinetic-Molecular Theory

Exercise $4.E.31$**

A 1-L sample of CO initially at 0 °C and 1 atm is heated to 546 K at constant volume.

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?

Answer available at the end of this section.

Exercise $4.E.32$*

Calculate the root-mean-square speed of nitrogen, $\mathrm{N_2}$, molecules in an air sample at 25 °C.

Answer available at the end of this section.

Exercise $4.E.33$**

What is the ratio of root-mean-square speed values for helium to xenon at 30 °C? Which has a higher root-mean-square speed and why?

Answer available at the end of this section.

Exercise $4.E.34$**

Consider two 1 L containers of gas, both at 1 atm and 298 K. One container contains He and one container contains $\mathrm{CH_4}$.

Compare the two gases in terms of

a. mass

b. density

c. average kinetic energy

d. average speed

e. collision frequency

Answer available at the end of this section.

Exercise $4.E.35$*

Which of the following gases diffuse more slowly than oxygen? $\mathrm{F_2}$, Ne, $\mathrm{N_2O}$, $\mathrm{C_2H_2}$, NO, $\mathrm{Cl_2}$, $\mathrm{H_2S}$

Answer available at the end of this section.

Additional Problems

Exercise $4.E.36$***

A 2.00 L flask originally contains 1.00 g of ethane ($\mathrm{C_2H_6}$) and 32.0 g of oxygen at 21°C. During ignition, the ethane reacts completely with oxygen to produce $\mathrm{CO_2}$ and water vapor, and the temperature of the flask increases to 200°C. Determine the total pressure before and after the reaction.

$$2\,\mathrm{C_2H_6}(g)+7\,\mathrm{O_2}(g) \longrightarrow 4\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(g)$$

Answer available at the end of this section.

Exercise $4.E.37$**

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer available at the end of this section.

Exercise $4.E.38$**

Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % $\mathrm{O_2}$ is not. If enough $\mathrm{O_2}$ is added to a cylinder of $\mathrm{H_2}$ at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive? Assume there is no change in temperature.

Answer available at the end of this section.

Exercise $4.E.39$***

A sample of a compound of xenon and fluorine, XeF_n, was put in a bulb with a pressure of 18 mmHg. Hydrogen gas, H_2, was added to the bulb until the pressure was 72 mmHg. Passage of an electric spark through the mixture caused a reaction to occur, producing Xe gas and HF. After the HF was removed by reaction with solid KOH, the final pressure of the Xe gas and unreacted H_2 gas in the bulb was 36 mmHg. What is the formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.) Assume temperature is constant.

Answer available at the end of this section.

Exercise $4.E.40$***

At 140°C, the pressure of a diatomic gas, X_2, in a 3.0 L flask is 6.267 atm. The mass of the gas is 88.7 g. What is the most likely identity of the gas?

Answer available at the end of this section.

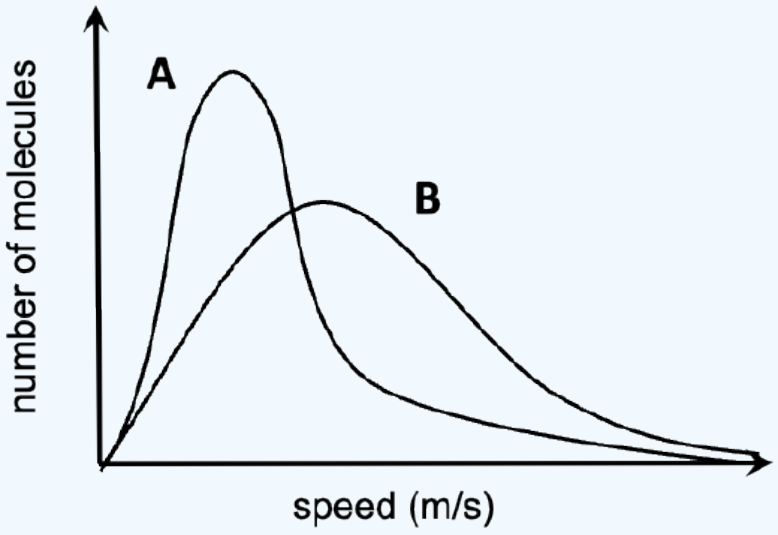
Exercise $4.E.41$**

What is the density of laughing gas, dinitrogen monoxide, $\mathrm{N}_2\mathrm{O}$, at a temperature of 325 K and a pressure of 113.0 kPa?

Answer available at the end of this section.

Exercise $4.E.42$**

The graph below shows the distribution of molecular speeds for two gases, A and B, at the same temperature.



Which of the following statements are true? Correct any incorrect statements

a) Gas B and Gas A have the same molar mass.
b) The average kinetic energy of Gas B is greater than that of Gas A.
c) The rate of effusion of Gas A would be greater than the rate of effusion of Gas B.
d) Increasing the temperature will shift both distributions to the right, to higher speeds.
e) The rate of diffusion of Gas A would be the same as the rate of diffusion of Gas B.

Answer available at the end of this section.

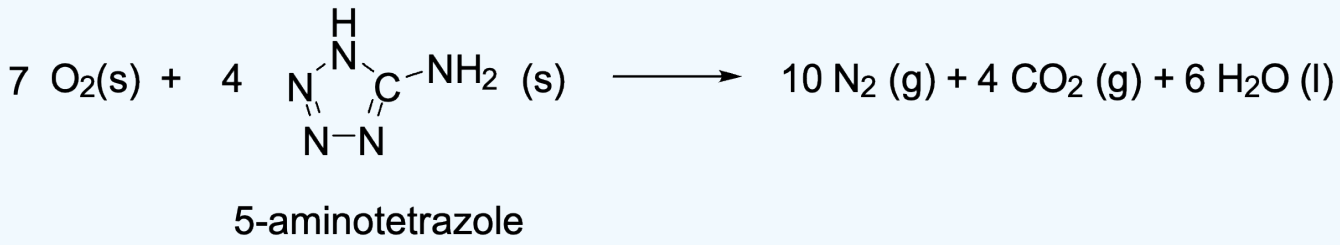
Exercise $4.E.43$

a) Sodium azide ($\mathrm{NaN_3}$) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2\,\mathrm{NaN_3\,(s)} \rightarrow 2\,\mathrm{Na\,(s)} + 3\,\mathrm{N_2\,(g)}$$

This reaction can be used to inflate the airbags in cars that cushion passengers during collisions. In airbags this reaction is initiated by an electrical impulse and results in the rapid evolution of gas. What volume of gas is formed from the decomposition of 130 g $\mathrm{NaN_3}$ (the mass used in a standard driver-side airbags) at 21°C and 1.00 atm?

b) Exposure to unreacted sodium azide and byproducts of this reaction can be hazardous, which has led chemists to develop new safer alternatives. One such alternative is 5-aminotetrazole, which upon full oxidation decomposes according to the chemical equation below:



5-aminotetrazole

i. How many moles of gas are required to inflate the airbag to 72.4 L at 21°C and 1.00 atm?

ii. How many moles of the gas mixture are $\mathrm{N_2}$?

iii. What mass of 5-aminotetrazole is needed to inflate the airbag to 72.4 L?

Answer a available at the end of this section.

Green Chemistry Connection

Toxicology of chemicals can be measured in many ways, including the Lethal Dose 50 (LD50). LD50 describes the dose required to kill 50% of the tested population. Therefore, a lower LD50 value indicates a more toxic substance.

For example, the LD50 value for sodium azide is 19 mg/kg, while 5-aminotetrazole has an LD50 value of 623 mg/kg. Given that the LD50 value for 5-aminotetrazole is 33 times higher than for sodium azide, 5-aminotetrazole is a greener and safer alternative to sodium azide in airbag inflation systems.

Answers

Exercise $4.E.1$**

a) gas < liquid < solid

For most substances, density increases from gas to liquid to solid. However, there are exceptions. Water, for example, is less dense as a solid (ice) than as a liquid.

b) solid < liquid < gas

Gases are much more compressible than liquids or solids. Solids are generally the least compressible.

c) solid < liquid < gas

Molecular motion increases with temperature and phase. In solids, particles vibrate in place; in liquids, they move more freely; and in gases, they move rapidly and randomly.

Exercise $4.E.2$**

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.

Exercise $4.E.3$*

$$102.3 \text{ kPa} \left(\frac{1 \text{ atm}}{101.325 \text{ kPa}} \right) = 1.010 \text{ atm}$$

$$102.3 \text{ kPa} \left(\frac{760 \text{ mmHg}}{101.325 \text{ kPa}} \right) = 767.3 \text{ mmHg}$$

Exercise $4.E.4$*

$$88.8 \text{ atm} \left(\frac{760 \text{ mmHg}}{1 \text{ atm}} \right) = 67500 \text{ mmHg}$$

Exercise $4.E.5$**

a. Converting from cm to mm, we obtain 264 mmHg as a height difference between two arms. Since this is a closed-end manometer, the height difference gives the pressure of the gas.

b.

$$264 \text{ mmHg} \left(\frac{1 \text{ atm}}{760 \text{ mmHg}} \right) = 0.347 \text{ atm}$$

Exercise $4.E.6$**

a. Converting from cm to mm, we obtain 137 mmHg as a height difference between two arms. The gas pressure is less than atmospheric pressure since the level of the mercury is higher on the left side (gas side) than the right side (open to atmosphere).

760 mmHg - 137 mmHg = 623 mmHg

b.

$$623 \text{ mmHg} \left(\frac{1 \text{ atm}}{760 \text{ mmHg}} \right) = 0.820 \text{ atm}$$

Exercise $4.E.7$*

As the bubbles rise, the pressure decreases, so their volume increases.

Exercise $4.E.8$*

$$V = \frac{nRT}{P} = \frac{(1.00\,mol)(0.08206\frac{L \cdot atm}{mol \cdot K})(150.0\,K)}{1.00\,atm} = 12.3\,L$$

Exercise $4.E.9$*

276 K

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$$

Since the sample of CO gas is the same $n_i = n_f$, so we cancel those from the equation.

$$\frac{P_i V_i}{\cancel{n_i} T_i} = \frac{P_f V_f}{\cancel{n_f} T_f}$$

Solving for T_i:

$T_i = \frac{P_i V_i T_f}{P_f V_f}$

Where:

$P_i = 744\ torr$

$V_i = 11.2\ L$

$P_f = 744\ torr$

$V_f = 13.3\ L$

$T_f = 328\ K$

$\frac{(744\,torr)(11.2\,L)(328\,K)}{(744\,torr)(13.3\,L)} = 276\ K$

Exercise $4.E.10$*

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$$

Since the sample of $\mathrm{H_2}$ gas is the same $n_i = n_f$ and there is no change in pressure, so P_i=P_f.

$$\frac{\cancel{P_i} V_i}{\cancel{n_i} T_i} = \frac{\cancel{P_f} V_f}{\cancel{n_f} T_f}$$

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

$$V_f = \frac{V_i T_f}{T_i} = \frac{(2.50\,L)(373\,K)}{(77\,K)} = 12.1\,L$$

Exercise $4.E.11$**

Use the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1.220\ atm)(4.3410\ L)}{(0.08206\frac{L \cdot atm}{mol \cdot K})(788.0\ K)} = 0.08190\ mol$$

Convert moles to grams using the molar mass of BF_3 (67.81 g/mol):

$$0.08190\ mol(67.81\frac{g}{mol}) = 5.553\ g$$

Exercise $4.E.12$*

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$

$n_i = n_f$, so we can cancel those from the equation:

$$\frac{P_iV_i}{\cancel{n_i}T_i} = \frac{P_fV_f}{\cancel{n_f}T_f}$$

$$P_f = \frac{P_iV_iT_f}{T_iV_f}$$

$$P_f = \frac{(0.981\ atm)(100.21\ L)(278\ K)}{(144.53\ L)(294\ K)} = 0.643\ atm$$

Exercise $4.E.13$**

359 K

Use the equation $PV = nRT$ and solve for T

$T = \frac{PV}{nR}$

Convert grams of I_2 to moles of I_2 and convert mL to L

$0.292\ g\ I_2 \times \frac{1\ mole\ I_2}{253.8\ g\ I_2} = 1.15 \times 10^{-3}\ mol\ I_2$

$73.3\ mL = 0.0733\ L$

Use these values along with $R = 0.08206\ \frac{atm \cdot L}{mol \cdot K}$ to solve for T

$$T = \frac{(0.462\ \cancel{atm})(0.0733\ \cancel{L})}{(1.15 \times 10^{-3}\ \cancel{mol})(0.08206\ \frac{\cancel{atm} \cdot \cancel{L}}{\cancel{mol} \cdot K})} = 359\ K$$

Exercise $4.E.14$**

To find the mass of butane, we need to find the moles of butane left in the cylinder:

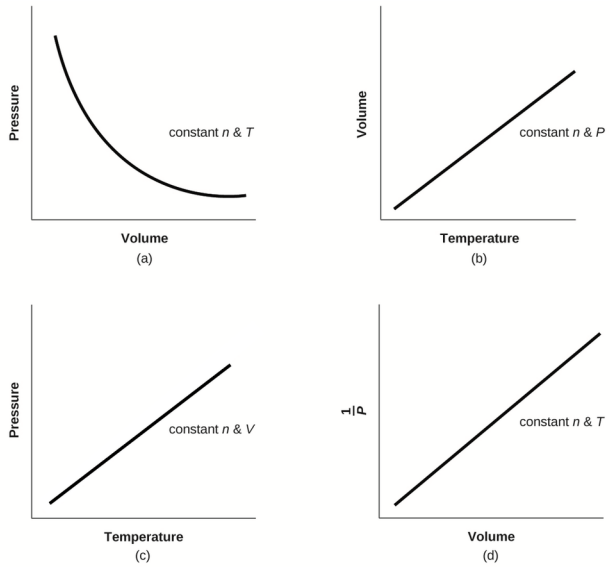
$$n = \frac{PV}{RT} = \frac{(0.983\ atm)(20.0\ L)}{(0.08206\frac{L \cdot atm}{mol \cdot K})(300\ K)} = 0.799\ mol$$

The molar mass of butane, 58.12 g/mol, can be used to find the mass.

$$0.799\ mol\ C_4H_{10}\ (58.12\frac{g}{mol}) = 46.4g$$

Exercise $4.E.15$**

For a gas exhibiting ideal behaviour:



Exercise $4.E.16$*

The pressure decreases by a factor of 3.

Exercise $4.E.17$**

Volume is predicted to increase. The addition of more gas (at the same volume) would result in more collisions and an increase in pressure. For pressure to remain constant, the volume would have to increase, so that the number of collisions per unit area of the balloon is the same. Increasing volume affects the collisions by increasing the surface area of the balloon and by increasing the average distance the He atoms have to travel to collide with the balloon wall.

Exercise $4.E.18$**

Before performing the calculation, predict whether you expect the pressure to increase or decrease with the change in volume.

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$

$n_i = n_f$ and $T_i = T_f$, so we can cancel those from the equation:

$$\frac{P_iV_i}{\cancel{n_i}\ \cancel{T_i}} = \frac{P_fV_f}{\cancel{n_f}\ \cancel{T_f}}$$

$$P_iV_i = P_fV_f$$

$$P_f = \frac{P_iV_i}{V_f} = \frac{(455\ mmHg)\frac{1\ atm}{760\ mmHg}(8.60\ L)}{(8.60\ L + 5.35\ L)} = 0.369\ atm$$

Don't forget to convert the pressure from mmHg to atm.

Exercise $4.E.19$**

First, find the number of breaths taken each day:

$$1\ \text{day}\left(\frac{24\ \text{h}}{\text{day}}\right)\left(\frac{60\ \text{min}}{\text{h}}\right)\left(\frac{20\ \text{breaths}}{\text{min}}\right) = 28800\ \text{breath/day}$$

Next, calculate the moles in each breath.

$$n = \frac{PV}{RT} = \frac{(0.997\ \text{atm})(0.310\ \text{L})}{(0.08206\frac{\text{L·atm}}{\text{mol·K}})\,(293\ \text{K})} = 0.0129\ \text{mol}$$

Finally, multiply to get the moles per day:

$$\left(0.0129\frac{\text{mol}}{\text{breath}}\right)\left(28800\frac{\text{breath}}{\text{day}}\right) = 370\frac{\text{mol}}{\text{day}}$$

Exercise $4.E.20$**

To find the density we need mass/volume, g/L. From the ideal gas equation, we can find moles/volume and then use the molar mass to find the density.

Rearranging the ideal gas equation:

$$\frac{n}{V} = \frac{P}{RT}$$

Paying attention to units, solve for n/V:

$$\frac{n}{V} = \frac{0.954\ atm}{(0.08206\frac{L\cdot atm}{mol\cdot K})\,(303\ K)} = 0.0384\frac{mol}{L}$$

Finally, use the molar mass to find the density:

$$0.0384\frac{\cancel{mol}}{L}\left(120.91\frac{g}{\cancel{mol}}\right) = 4.64\frac{g}{L}$$

Exercise $4.E.21$**

30.0 g/mol

Convert Torr to atm and °C to K

$307\ \ Torr = 0.404\ \ atm$

$26\ \ ^\circ C = 299\ \ K$

2.) Use the equation $PV = nRT$ and solve for n

$n = \frac{PV}{RT}$

$$n = \frac{(0.404\ \cancel{atm})(0.100\ \cancel{L})}{(0.08206\frac{\cancel{atm}\cdot\cancel{L}}{mol\cdot\cancel{K}})(299\cancel{K})} = 0.00165\ \ mol$$

3.) Then divide grams by the number of moles to obtain the molar mass:

$\frac{0.0494\ g}{0.00165\ mol} = 30.0\frac{g}{mol}$

Exercise $4.E.22$**

Convert units as needed:

$777\ \ Torr = 1.02\ \ atm$

$126\ \ ^\circ C = 399\ \ K$

$125\ \ mL = 0.125\ \ L$

2.) Use the equation $PV = nRT$ and solve for n

$n = \frac{PV}{RT}$

$$n = \frac{(1.02\ \cancel{atm})(0.125\ \cancel{L})}{(0.08206\frac{\cancel{atm}\cdot\cancel{L}}{mol\cdot\cancel{K}})(399\cancel{K})} = 0.00390\ mol$$

3.) Then divide grams by the number of moles to obtain the molar mass:

$$\frac{0.281\ g}{0.00390\ mol} = 72.0\frac{g}{mol}$$

Exercise $4.E.23$**

We know the pressure and temperature, which allows us to find how many moles 1 L of this gas contains (mol/L). We can use this, along with the density, to find the molar mass.

Paying attention to units, solve for n/V:

$$\frac{n}{V} = \frac{1.00\ atm}{(0.08206\frac{L\cdot atm}{mol\cdot K})\,(273.15\ K)} = 0.0446\frac{mol}{L}$$

A 1 L sample would have a mass of 3.93 g (from the density) and contain 0.0446 mol (from the calculation we just did).

$$\frac{3.93\ g}{0.0446\ mol} = 88.1\ g/mol$$

The gas is most likely PF_3.

Exercise $4.E.24$**

First find the moles of HgO and the moles of O_2 produced in the reaction:

$$5.36\text{ g HgO}\left(\frac{\text{mol}}{216.59\text{ g}}\right)\left(\frac{1\text{ mol }O_2}{2\text{ mol HgO}}\right) = 0.0124\text{ mol }O_2$$

Once we have the moles of O_2 produced, we can use the ideal gas equation to find the volume of the gas:

$$V = \frac{nRT}{P} = \frac{(0.0124\text{ mol})(0.08206\frac{\text{L·atm}}{\text{mol·K}})(296\text{ K})}{0.975\text{ atm}} = 0.309\text{ L}$$

Exercise $4.E.25$**

First find the moles of CCl_2F_2 and the moles of H_2 needed to react with the CCl_2F_2:

$$1.000\times10^3\text{ kg }CCl_2F_2\left(\frac{1000\text{ g}}{\text{kg}}\right)\left(\frac{\text{mol}}{120.91\text{ g}}\right)\left(\frac{4\text{ mol }H_2}{1\text{ mol }CCl_2F_2}\right) = 33082\text{ mol }H_2$$

Once we have the moles of H_2 produced, we can use the ideal gas equation to find the volume of the gas:

$$V = \frac{nRT}{P} = \frac{(33082\text{ mol})(0.08206\frac{\text{L·atm}}{\text{mol·K}})(308.7\text{ K})}{225\text{ atm}} = 3.72\times10^3\text{ L}$$

Exercise $4.E.26$**

Since the temperature and pressure are constant, the volumes of the gases are directly proportional to the number of moles present:

$$V = \frac{nRT}{P} = constant\times n$$

This means we can consider the stoichiometry of the reaction in terms of volumes:

$$12.00\text{ L }C_2H_6\left(\frac{7\text{ mol }O_2}{2\text{ mol }C_2H_6}\right) = 42.00\text{ L }O_2$$

Exercise $4.E.27$**

We can find the total pressure from the total moles of gas. First, convert the mass of each gas to moles and then use the ideal gas equation to find pressure:

$$350\text{ g }CO_2\left(\frac{\text{mol}}{44.01\text{ g}}\right) = 7.95\text{ mol}$$

$$805\text{ g }O_2\left(\frac{\text{mol}}{32.0\text{ g}}\right) = 25.2\text{ mol}$$

$$4880\text{ g }N_2\left(\frac{\text{mol}}{28.02\text{ g}}\right) = 174.2\text{ mol}$$

$$n_{tot} = 7.95\text{ mol} + 25.2\text{ mol} + 174.2\text{ mol} = 207.4\text{ mol}$$

$$P_{tot} = \frac{n_{tot}RT}{V} = \frac{(207.4\text{ mol})(0.08206\frac{\text{L·atm}}{\text{mol·K}})\,(298\text{ K})}{36.0\text{ L}} = 141\text{ atm}$$

$$\chi_A = \frac{\text{mol}_A}{\text{mol}_{tot}}$$

$$\chi_{O_2} = \frac{25.2\text{ mol}}{207.4\text{ mol}} = 0.122$$

$$P_A = \chi_A\times P_{tot}$$

$$P_{O_2} = (0.122)(141\text{ atm}) = 17.2\text{ atm}$$

Exercise $4.E.28$*

The percentages can be converted to mole fractions. 90.0% CH_4 means that the mole fraction of CH_4 is 0.900.

$$P_A = \chi_A\times P_{tot}$$

$$P_{CH_4} = 0.900(3.03\ atm) = 2.73\ atm$$

$$P_{C_2H_6} = 0.089(3.03\ atm) = 0.27\ atm$$

$$P_{C_3H_8} = 0.011(3.03\ atm) = 0.033\ atm$$

Exercise $4.E.29$**

Because gases act independently of each other, we can determine the resulting final pressures of each gas (to reflect the change in volume) and then add the two resulting pressures together to get the final pressure. The total final volume is 2.00 L + 5.00 L = 7.00 L. First, determine the final pressure of N_2:

(2.50 atm)(2.00 L) = P_f(7.00 L)

Solving for P_f, we get P_f = 0.714 atm = partial pressure of N_2.

Now we do the same thing for the He:

(1.90 atm)(5.00 L) = P_f(7.00 L) P_f = 1.36 atm = partial pressure of He

The total pressure is the sum of the two partial pressures:

P_{tot} = 0.714 atm + 1.36 atm = 2.07 atm

Exercise $4.E.30$*

There are more particles of H_2 than of Ar, so H_2 has the higher mole fraction and partial pressure.

Exercise $4.E.31$**

a. The number of collisions per unit area of the container wall increases.

Since the gas is heated at constant volume, the molecules move faster and collide with the container walls more often. This leads to more frequent collisions per unit area.

b. The average kinetic energy increases.

The average kinetic energy of a gas is directly proportional to its absolute temperature (in kelvin).

c. The root mean square speed increases.

The rms speed is proportional to the square root of the temperature. Since the temperature increases, the rms speed increases as well.

Exercise $4.E.32$*

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathscr{M}}}$$

$$u_{\text{rms}} = \sqrt{\frac{3(8.314 \frac{\cancel{kg} \cdot m^2}{\cancel{mol} \cdot s^2 \cdot \cancel{K}})(298 \cancel{K})}{28.02 \frac{\cancel{g}}{\cancel{mol}}} \left(\frac{1000 \cancel{g}}{\cancel{kg}}\right)} = 515 m/s$$

Exercise $4.E.33$**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathscr{M}}}$$

$$u_{\text{rmsHe}} = \sqrt{\frac{3RT}{\mathscr{M}_{He}}}$$

$$u_{\text{rmsXe}} = \sqrt{\frac{3RT}{\mathscr{M}_{Xe}}}$$

$$\frac{u_{\text{rmsHe}}}{u_{\text{rmsXe}}} = \frac{\sqrt{\frac{3RT}{\mathscr{M}_{He}}}}{\sqrt{\frac{3RT}{\mathscr{M}_{Xe}}}}$$

$$\frac{u_{\text{rmsHe}}}{u_{\text{rmsXe}}} = \frac{\sqrt{\frac{\cancel{3RT}}{\mathscr{M}_{He}}}}{\sqrt{\frac{\cancel{3RT}}{\mathscr{M}_{Xe}}}} = \sqrt{\frac{\mathscr{M}_{Xe}}{\mathscr{M}_{He}}} = \sqrt{\frac{131.3\ g/mol}{4.003\ g/mol}} = 5.73$$

He has a higher root-mean-square speed by a factor of 5.73 compared to Xe. He is faster because it has a smaller molar mass.

Exercise $4.E.34$**

a. Since the volume, temperature, and pressure of the two gases are the same, they have the same number of moles. Since CH_4 has a larger molar mass, the mass is greater for the CH_4 gas.

b. Given the volume is the same for the two gases, the CH_4 gas has a higher density since it has a greater mass.

c. Both gases are at the same temperature, so their average kinetic energies are the same.

d. At the same temperature, the lighter gas, He, moves faster on average.

e. The collision frequency is greater for He because it has a greater average speed.

Exercise $4.E.35$*

The rate of diffusion is proportional to the speed. Heavier gases move more slowly. Any gas with a higher molar mass than O_2 will diffuse more slowly.

F_2, N_2O, Cl_2, H_2S

Exercise $4.E.36$***

Before reaction:

We can find the total pressure by finding the total moles of gas present:

$$1.00\ \text{g}\ C_2H_6 \left(\frac{\text{mol}}{30.07\ \text{g}}\right) = 0.0333\ \text{mol}\ C_2H_6$$

$$32.0\ \text{g}O_2 \left(\frac{\text{mol}}{32.0\ \text{g}}\right) = 1.00\ \text{mol}$$

$$n_{\text{tot}} = 0.0333\ \text{mol} + 1.00\ \text{mol} = 1.03\ \text{mol}$$

$$P_{\text{tot}} = \frac{n_{\text{tot}}RT}{V} = \frac{(1.03\ \text{mol})(0.08206\ \frac{\text{L·atm}}{\text{mol·K}})(294\ \text{K})}{2.00\ \text{L}} = 12.5\ \text{atm}$$

After the reaction:

We need to know how many moles are present of each reactant and product.

All of the C_2H_6 reacts since there is a big excess of O_2, so C_2H_6 does not contribute to the pressure.

The amount of O_2 that reacts can be found as follows:

$$0.0333 \text{ mol } C_2H_6 \left(\frac{7 \text{ mol } O_2}{2 \text{ mol } C_2H_6} \right) = 0.117 \text{ mol } O_2$$

So the amount left after the reaction is 1.00 mol - 0.117 mol = 0.883 mol O_2.

CO_2 and H_2O gases are formed from the reaction:

$$0.0333 \text{ mol } C_2H_6 \left(\frac{4 \text{ mol } CO_2}{2 \text{ mol } C_2H_6} \right) = 0.0666 \text{ mol } CO_2$$

$$0.0333 \text{ mol } C_2H_6 \left(\frac{6 \text{ mol } H_2O}{2 \text{ mol } C_2H_6} \right) = 0.0999 \text{ mol } H_2O$$

We can find the total moles to find the total pressure. Don't forget that the temperature has also increased.

$$n_{\text{tot}} = 0.883 \text{ mol} + 0.0666 \text{ mol} + 0.0999 \text{ mol} = 1.05 \text{ mol}$$

$$P_{\text{tot}} = \frac{n_{\text{tot}} RT}{V} = \frac{(1.05 \text{ mol})(0.08206 \frac{\text{L·atm}}{\text{mol·K}})\,(473 \text{ K})}{2.00 \text{ L}} = 20.3 \text{ atm}$$

Exercise $4.E.37$**

We can find out how many moles of Ar are needed to fill each lightbulb:

$$n = \frac{PV}{RT} = \frac{(1.00\,atm)(0.0150\,L)}{(0.08206 \frac{L \cdot atm}{mol \cdot K})(298\,K)} = 6.13 \times 10^{-4}\,mol$$

We can also calculate the moles of Ar in the cylinder:

$$n = \frac{PV}{RT} = \frac{(145\,atm)(0.400\,L)}{(0.08206 \frac{L \cdot atm}{mol \cdot K})(283\,K)} = 2.50\,mol$$

We take the moles from the cylinder and divide by the moles needed for each light bulb to find how many lightbulbs can be filled:

$$\frac{2.50\,mol}{6.13 \times 10^{-4}\,mol} = 4.08 \times 10^3 \text{ lightbulbs}$$

Exercise $4.E.38$**

To determine if the mixture is explosive, we need to find the mole fraction of O_2. We can write the mole fraction as a ratio of the pressure of O_2 to the total pressure, since volume and temperature are constant:

$$\chi_A = \frac{\text{mol}_A}{\text{mol}_{tot}} == \frac{\text{P}_A}{\text{P}_{tot}}$$

The pressure of O_2 can be found by subtracting the pressure of H_2 from the total pressure (since the gas mixture consists of only those two gases):

$$P_{O_2} = 34.5\,atm - 33.2\,atm = 1.3\,atm$$

$$\chi_{O_2} = \frac{1.3\,atm}{34.5\,atm} = 0.038$$

The gas mixture contains 3.8% O_2, which is greater than the threshold, so it is explosive.

Exercise $4.E.39$***

We can set up an equation as follows:

$XeF_n(g) + \frac{n}{2}H_2(g) \rightarrow Xe(g) + nHF(g)$

Initially, we have 18 mmHg of XeF_n and 54 mmHg of H_2 (72 mmHg - 18 mmHg).

After the reaction, we have unreacted H_2 gas, meaning that XeF_n is the limiting reactant and reacts completely. Since each XeF_n contains one Xe, we form 18 mmHg of Xe (because we had 18 mmHg of XeF_n). That means there is 18 mmHg of H_2 leftover (36 mmHg - 18 mmHg), so 36 mmHg (54 mmHg initially - 18 mmHg leftover) of H_2 reacted with 18 mmHg of XeF_n or twice as much H_2 as XeF_n:

$XeF_n(g) + 2H_2(g) \rightarrow Xe(g) + 4HF(g)$

For this to be true, n must be equal to 4, so the formula is XeF_4.

Exercise $4.E.40$***

To determine the identity of the gas, we need to determine the molar mass, g/mol. We have the mass in the question, so we will use the ideal gas law to determine the number of moles.

$$n = \frac{PV}{RT}$$

$$n = \frac{(6.267\ \cancel{atm})(3.0\ \cancel{L})}{(0.08206 \frac{\cancel{atm} \cdot \cancel{L}}{mol \cdot \cancel{K}})(413\cancel{K})} = 0.555\ mol$$

Then divide grams by the number of moles to obtain the molar mass:

$$\frac{88.7\,g}{0.555\,mol} = 160 \frac{g}{mol}$$

Each atom in X_2 has a mass of 80 g/mol, making the gas likely to be Br_2.

Video solution

Exercise $4.E.41$**

To find the density we need mass/volume, g/L. From the ideal gas equation, we can find moles/volume and then use the molar mass to find the density.

Rearranging the ideal gas equation:

$$\frac{n}{V} = \frac{P}{RT}$$

Paying attention to units, solve for n/V:

$$\frac{n}{V} = \frac{(113.0\text{ kPa})\left(\frac{1\text{ atm}}{101.325\text{ kPa}}\right)}{\left(0.08206\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(325\text{ K})} = 0.0418\frac{\text{mol}}{\text{L}}$$

Finally, use the molar mass to find the density:

$$0.0418\frac{\cancel{\text{mol}}}{\text{L}}\left(44.02\frac{\text{g}}{\cancel{\text{mol}}}\right) = 1.84\frac{\text{g}}{\text{L}}$$

Exercise $4.E.42$**

a) False; Since Gas B moves faster than Gas A, it must have a lower molar mass.

b) False; Since temperature is the same, both gases have the same average kinetic energy.

c) False; The rate of effusion is proportional to the speed. Since Gas B moves faster, Gas B will have the higher rate of effusion.

d) True

e) False; The rate of diffusion is proportional to the speed. Since Gas B moves faster, Gas B will have the higher rate of effusion.

Exercise $4.E.43$

From the stoichiometry of the reaction:

$$\frac{130\text{ g NaN}_3}{(22.99+3\times14.01)\text{ g/mol}}\times\frac{3\text{ mol N}_2}{2\text{ mol NaN}_3} = 3.00\text{ mol}$$

$$V = \frac{nRT}{P}$$

$$V = \frac{3.00\text{ mol}\times0.08206\text{ L}\cdot\text{atm mol}^{-1}\text{ K}^{-1}\times294\text{ K}}{1.00\text{ atm}}$$

$$V = 72.4\text{ L}$$

i.

$$n = \frac{PV}{RT}$$

$$n = \frac{1.00\text{ atm}\times72.4\text{ L}}{0.08206\text{ L}\cdot\text{atm mol}^{-1}\text{ K}^{-1}\times294\text{ K}}$$

$n = 3.00$ mol This is the total moles of gases.

ii. According to the balanced equation, every 4 mol of 5-aminotetrazole produces 10 mol N_2 and 4 mol CO_2, for a total of 14 mol gas.

$$n(\text{N}_2) = \frac{10\text{ mol N}_2}{10\text{ mol N}_2+4\text{ mol CO}_2}\times3.00\text{ mol}$$

$$n(\text{N}_2) = 2.14\text{ mol}$$

iii. From the reaction stoichiometry:

$$2.14\text{ mol N}_2\times\frac{2\text{ mol 5AT}}{5\text{ mol N}_2} = 0.857\text{ mol 5AT}$$

$$0.857\text{ mol 5AT}\times(12.01+3\times1.00+5\times14.01)\text{ g/mol}$$

$$= 72.9\text{ g}$$

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5: THERMOCHEMISTRY

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5.1: Introduction

When Calories Become Clues: What Thermochemistry Teaches Us About Healing and Nutrition



Figure 5.1.1**:** A graphic with basic facts about Carla Prado, Brazilian-born nutritionist who uses whole body calorimetry to study how different health conditions affect how the human body uses and expends energy. Dr. Prado then uses this information to suggest nutritional tactics to aid recovery. Image from University of Alberta; copyright 2025 University of Alberta.

Thermochemistry explores the energy changes that accompany chemical and physical processes. Every transformation, from the synthesis of a molecule to digestion of your lunch, involves the exchange of heat. In many cases, the energy produced by a reaction is more important than the products formed. For example, in fuel combustion, our goal is often to extract as much usable energy as possible to power other systems. Thermochemical principles help us understand how energy is transferred, what it tells us about a system, and how we can harness it.

Later in this chapter, we will discuss calorimetry, a technique used to measure heat flow. While it is often applied to chemical reactions or heat transfer between objects of different temperatures, calorimetry also has applications in human health. Dr. Carla Prado, a Brazilian-born nutritional scientist and expert in body composition and metabolism, uses a technique called whole-body calorimetry to investigate how people with different health conditions expend energy.

Whole-body calorimetry chambers measure the heat exchanged by the body to determine someone's metabolic rate. These chambers precisely monitor oxygen consumption, carbon dioxide production, and thermal output, converting these physical data into an energy profile of the person inside. Prado and her research group then use this information to study the effect of different conditions on the body and guide the design of nutritional interventions to improve patient recovery. Her research group has applied this process to patients with cancer, chronic illness, obesity, and, most recently, postpartum women. Prado's work has shown that postpartum women, especially those who have undergone C-sections, often face significant nutritional and energy challenges that traditional guidelines overlook.



Figure 5.1.2**:** Photo of one of the whole body calorimeter rooms at the University of Alberta's Human Nutrition Research Unit. While it l mostly like a regular room, it is sealed and connected to an air flow system that flushes "fresh air" through for precise monitoring of ox consumption and carbon dioxide production by the person inside. The room also possesses specialized ports for blood draws or food pa that minimize the loss of air from the room. Participants can be monitored precisely for longer periods of time, both at rest and wh conducting physical activity. Image from University of Alberta; copyright 2025 University of Alberta.

By applying the laws of thermochemistry to human metabolism, Dr. Prado's research has helped shape personalized nutrition plans that reduce complications, support healing, and improve long-term health outcomes. Her work is a striking example of how enthalpy, energy balance, and calorimetry are more than abstract concepts—they are tools that can transform healthcare and quality of life. In this chapter, we will explore the same core principles that underpin Prado's research: energy, enthalpy, and calorimetry, with a focus on their role in chemical transformations.

Sources:

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5.2: Energy and Its Conversion

Learning Objectives

- Define energy and distinguish between different forms of energy.
- Describe how energy is transferred as heat and explain the concept of energy conservation

What is Energy?

Energy is the capacity to do work or transfer heat. Work is defined as the transfer of energy that occurs when an object is moved against an opposing force. For example, lifting a book from the floor requires you to apply a force against gravity, so work is done. When you inflate a tire, energy is transferred as work because the added air exerts a force on the inner wall of the tire. For CHM 135, we will focus on pressure-volume work which is introduced in the next section.

Energy is fundamental to many aspects of our lives (Figure 5.2.1). The nutrients in food—proteins, fats, and carbohydrates—undergo metabolic reactions that provide the energy necessary for bodily functions. We utilize various fuels, such as gasoline, natural gas, and coal, to produce energy for transportation, heating, and electricity generation. Industrial processes consume energy to transform raw materials like iron and aluminum into useful products, including cars, skyscrapers, and bridges.

Thermodynamics is the study of energy and its transformations. Within this field, thermochemistry focuses on the energy changes that occur during chemical and physical processes. The principles of thermochemistry are widely applicable across scientific and technical disciplines. For example:

- Food Science: Determining the energy content of foods.
- Biology: Studying the energetics of living organisms, such as the metabolic conversion of sugar into carbon dioxide and water.
- Energy Industry: Developing methods to produce energy for commercial and personal use.
- Engineering: Improving energy efficiency, optimizing heating and cooling systems, refrigerating perishables, and meeting the energy demands of electronics.

Understanding thermochemical principles is essential for chemistry, physics, biology, geology, engineering, and many other scientific fields.



Figure 5.2.1: Energy and Chemical Changes in Daily Life : (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 used to make 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)

Forms and Conversion of Energy

Energy exists in various forms (Figure 5.2.2), including:

- Thermal energy – the motion of atoms and molecules
- Radiant energy – the energy carried by electromagnetic waves (for example, objects left in the sunshine become warm because electromagnetic radiation is absorbed and converted to thermal energy.)
- Nuclear energy – the energy stored in the nucleus of an atom, which can be released during nuclear reactions
- Chemical energy – the energy associated with the arrangement of atoms in a substance

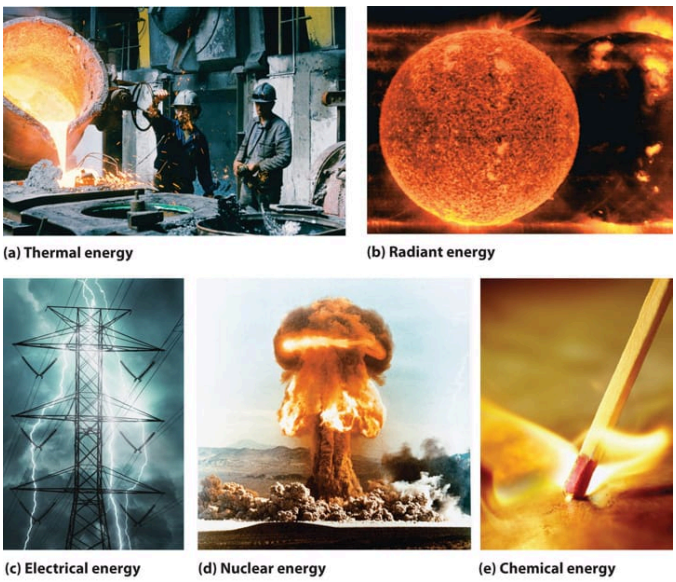


Figure 5.2.2: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.

These can be categorized into two main types:

- Kinetic Energy: the energy of motion.
- Potential Energy: stored energy due to position or arrangement.

Nuclear and chemical energies are forms of potential energy. For example, a battery contains chemical potential energy because chemical reactions occur to produce electricity, which can then be used to perform work (more details in Chapter 11!).

Energy can also be converted from one form to another. For example, water at the top of a waterfall or dam has gravitational potential energy because of its height. As the water flows downward, it gains kinetic energy, which is used to turn turbines and generate electricity in a hydroelectric plant (Figure 5.2.3).

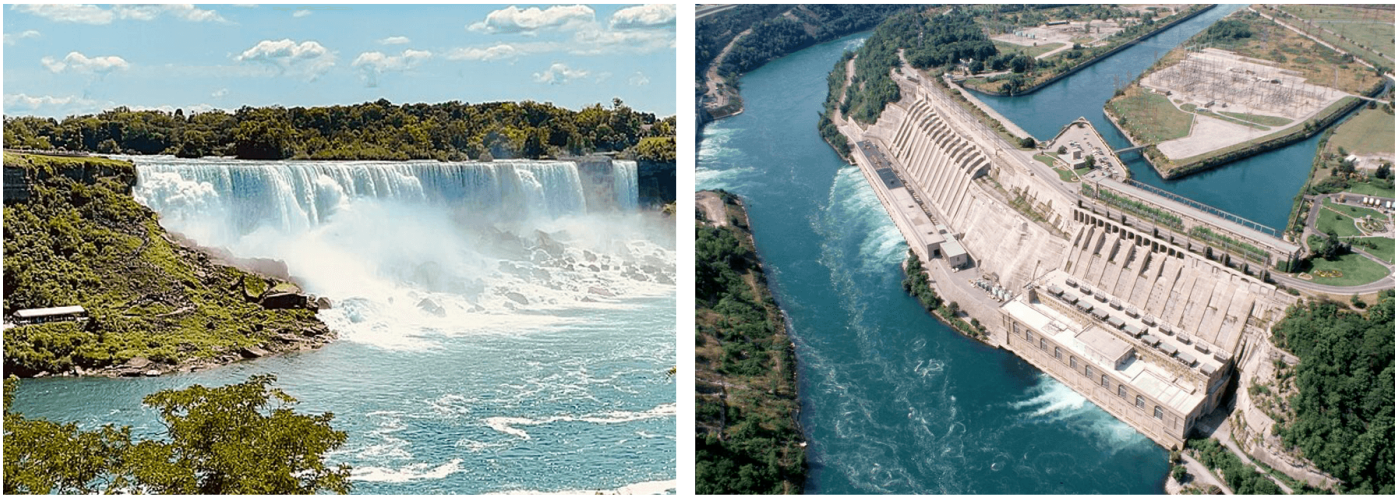


Figure 5.2.3: a) Water at the top of Niagara Falls (Ontario, Canada) possesses gravitational potential energy.
(b) As it descends, this energy is converted into kinetic energy, which is harnessed by the Sir Adam Beck Generating Station (Ontario, Canada) to produce electricity.
Image credits: (a): By SneakyFlamingo - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/inde...urid=161030874(b): Ontario Power Generation, CC BY 2.0 <https://creativecommons.org/licenses/by/2.0>, via Wikimedia Commons

The **law of conservation of energy**, also known as the first law of thermodynamics, states that energy cannot be created or destroyed; it can only change forms. The total energy before and after a transformation remains constant.

Thermal Energy, Temperature, and Heat

In thermochemistry, we're especially interested in thermal energy, the energy associated with the motion of atoms and molecules, and how it is transferred as heat during chemical and physical changes.

- Thermal energy is the kinetic energy of randomly moving atoms and molecules.
- Temperature (*T*) is a measure of the average kinetic energy of particles in a substance.
- Heat (*q*) is the transfer of thermal energy between objects at different temperatures.

Heat flows naturally from warmer objects to cooler ones until both reach the same temperature, a state called thermal equilibrium. For example, when a hot metal object is placed in cool water, the metal cools down and the water warms up. Thermal energy flows from the metal to the water until they reach the same temperature (Figure 5.2.4).

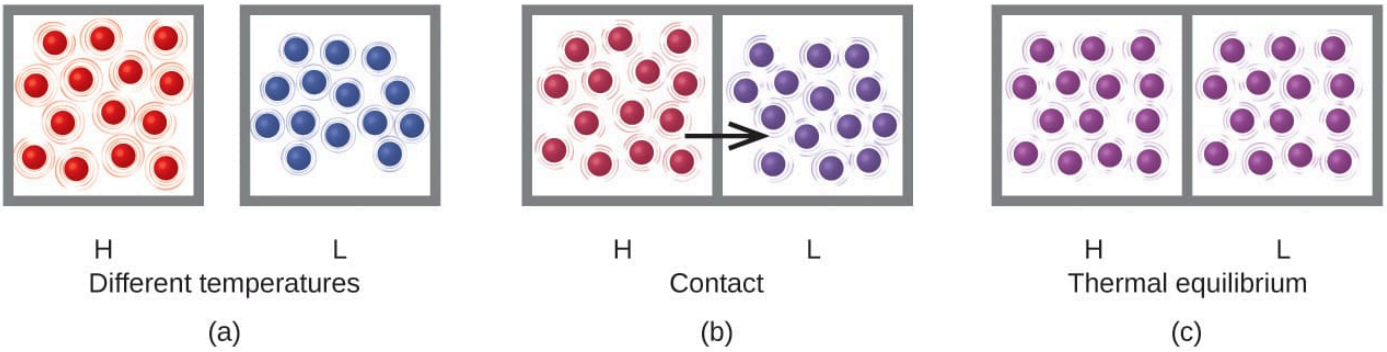


Figure 5.2.4: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature and their molecules have the same average kinetic energy.

Units of Energy

In chemistry, we use energy units that apply to all types of energy, whether it's thermal, chemical, or mechanical.

The SI unit of energy is the joule (J), defined as: $1\ J = 1\ kg \cdot m^2/s^2$

Because a joule is a relatively small amount of energy, we often use kilojoules (kJ) in chemistry:$1\ kJ = 1000\ J$

Another common unit is the calorie (cal), which was originally defined as the amount of energy needed to raise the temperature of 1 gram of water by 1°C. The conversion is: $1\ cal = 4.184\ J$

Although the calorie still appears in some contexts (like food energy), we will use joules and kilojoules throughout this textbook.

Summary

Energy is the capacity to do work or transfer heat. Energy exists in different forms, including thermal, chemical, nuclear, and radiant energy.

Energy is classified as either kinetic energy, the energy of motion, or potential energy, stored energy due to position or arrangement.

Heat (q) is the transfer of thermal energy between objects at different temperatures.

Temperature is a measure of the average kinetic energy of particles in a substance.

Energy is conserved: it cannot be created or destroyed, only transformed from one form to another.

The SI unit of energy is the joule (J). We also use kilojoules (kJ).

Glossary

chemical energy
: The energy associated with the arrangement of atoms in a substance.

energy
: The capacity to supply heat or do work.

heat (q)
: The transfer of thermal energy between two bodies.

nuclear energy
: The energy stored in the nucleus of an atom, which can be released during nuclear reactions.

potential energy
: Stored energy due to position or arrangement.

radiant energy
: The energy carried by electromagnetic waves.

temperature
: Intensive property of matter that is a quantitative measure of "hotness" and "coldness".

thermal energy
: The kinetic energy associated with the random motion of atoms and molecules.

thermochemistry
: The study of measuring the amount of heat energy absorbed or released during a chemical reaction or a physical change.

work (w)

The energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force.

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5.3: The First Law of Thermodynamics

Learning Objectives

- Define the system and surroundings in a thermodynamic context.
- Explain the first law of thermodynamics.
- Distinguish between state functions and path functions, giving examples of each.
- Relate the change in internal energy of the system to heat flow and work using the correct sign convention.
- Calculate pressure-volume work.

In thermodynamics, it is useful to distinguish between the system and its surroundings. The system refers to the specific part of the universe we are studying, such as the reactants and products in a chemical reaction. The surroundings include everything else. For example, Figure $5.3.1$ shows the reactants and products of a chemical reaction as the system and the surroundings as everything outside the system, including the flask where the reaction occurs. This distinction allows us to determine changes in energy in the system by observing the surroundings, since energy flows between the two. According to the law of conservation of energy, the total energy of the system and surroundings remains constant.

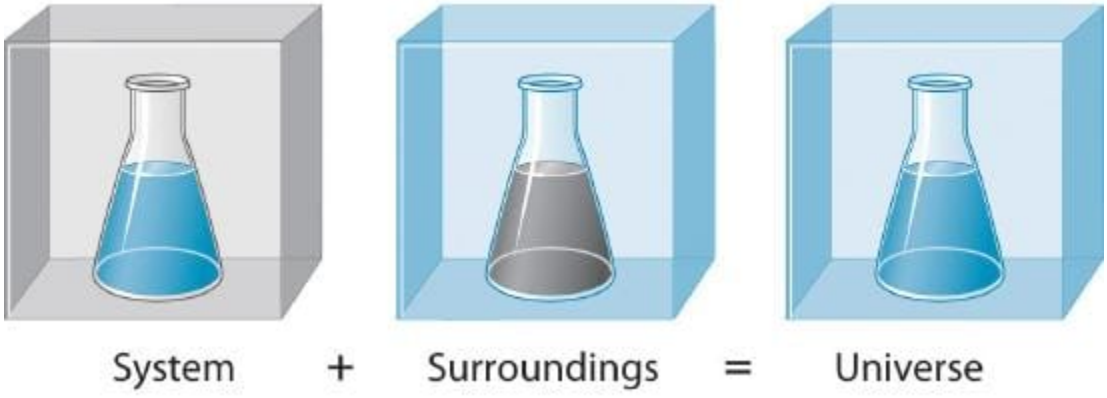


Figure $5.3.1$: A System and its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Each particle in the system has both potential and kinetic energy. The total of these energies is called the internal energy (E) of the system. In practice, we are often interested in changes in internal energy, rather than the total value, since absolute internal energy is difficult to measure. The change in internal energy is written as:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

For chemical reactions, this becomes:

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

By convention, energy changes are described from the system's point of view. Energy gained by the system from the surroundings is positive. Energy lost by the system to the surroundings is negative. Figure $5.3.2$ illustrates these ideas. In panel A, energy flows into the system, increasing its internal energy, and so ΔE is positive ($\Delta E > 0$). In panel B, energy flows out of the system, decreasing its internal energy, and so ΔE is negative ($\Delta E < 0$). The arrows show the direction of energy flow, and the signs indicate whether energy is gained or lost by the system.

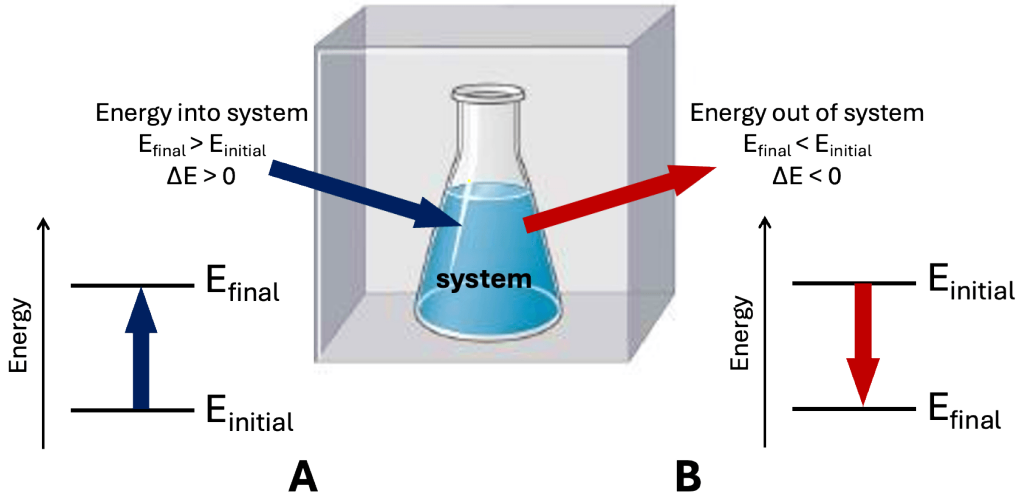


Figure 5.3.2: Energy flow between the system (the reactants in the flask) and the surroundings (everything else). (A) When energy flows into the system from the surroundings, the internal energy increases and ΔE is positive. (B) When energy flows out of the system into the surroundings, the internal energy decreases and ΔE is negative.

The state of a system is a complete description of its condition at a given moment, including properties like temperature, pressure, volume, amount of matter, and chemical composition. A state function is a property that depends only on the current state of the system, not on how the system reached that state. It is a *function* of the the *state* of the system. Examples of state functions include internal energy, temperature, pressure, and volume.

In contrast, heat and work are path functions as their values depend on the specific process or path taken to reach a particular state.

For example, a car's elevation at the top level of a parking garage is the same no matter how it got there - whether it was driven up a ramp, lifted by a crane, or carried up in pieces (Figure 5.3.3). However, the amount of work required and the distance traveled would be different for each path. Elevation is a state function, but distance and work are not.

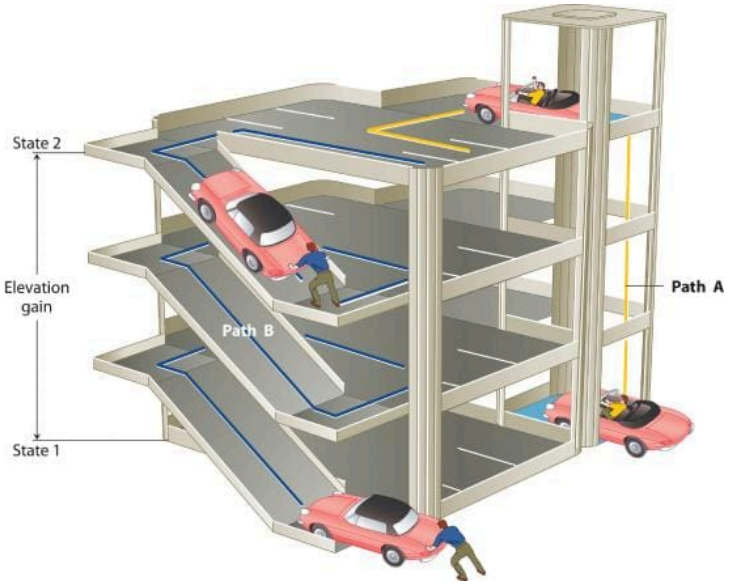


Figure 5.3.3: Elevation as an example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions.

The First Law

The first law of thermodynamics, also known as the law of energy conservation, states that energy cannot be created or destroyed; it can only be transformed from one form to another. In the context of thermodynamics, this law emphasizes that the total energy of the universe remains constant. Mathematically, this is expressed as:

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0 \tag{5.3.1}$$

$$\Delta E_{sys} = -\Delta E_{surr} \tag{5.3.2}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Because the total energy of the universe is constant, the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

Energy can be transferred between the system and the surroundings in two forms, heat (q) and work (w). The total change in the internal energy of the system is the sum of the energy transferred as heat and work:

$$\Delta E_{sys} = q + w \tag{5.3.3}$$

It's important to note that while heat and work are not state functions (they depend on the path taken), their sum, the change in internal energy (ΔE), is a state function. This means that the change in internal energy depends only on the initial and final states of the system, not on how the change occurred. Designers of machines that convert energy into work (e.g. engines) try to maximize the work output and minimize energy lost as heat. An example is the combustion of fuels to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed.

Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

We can determine ΔE for any process if we can measure both q and w. Heat, q, can often be determined by measuring the temperature change (ΔT) of the surroundings. Work, w, is a type of energy that comes in many forms, including electrical work which we will see at the end of the course. Mechanical work is the product of force F and distance d:

$$w = F \times d$$

The larger the required force, or the longer the distance an object is moved, the more work is done on it.

A common type of mechanical work in chemical processes is pressure-volume (PV) or expansion work, which occurs when the volume of a gas changes against an external pressure. At constant external pressure, the work done by the system is given by:

$$w = -P\Delta V \tag{5.3.4}$$

Here, P represents the external pressure, and ΔV is the change in volume. The negative sign indicates that when the system expands ($\Delta V > 0$), it does work on the surroundings, resulting in a loss of internal energy. Conversely, when the system is compressed ($\Delta V < 0$), work is done on the system by the surroundings, increasing its internal energy. A conversion factor is needed for the units to work out: 1 L·atm = 101.3 J.

Figure $5.3.4$ illustrates a reaction taking place inside a container with a movable piston. In this case, the products of the reaction have a greater volume than the reactants causing the piston to push outward against atmospheric pressure, doing work on the surroundings.

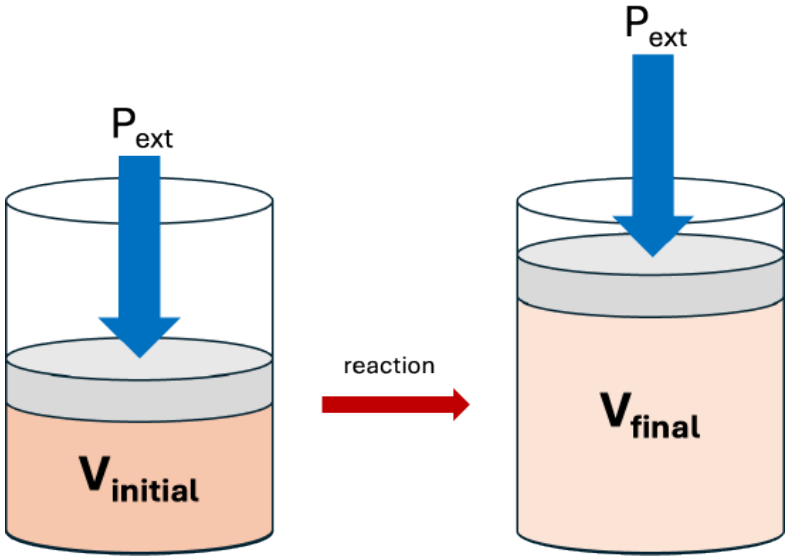


Figure 5.3.4: Expansion work in a chemical reaction. The increase in volume from the reaction forces the piston to move against atmospheric pressure. Work is done on the surroundings and energy is lost by the system.

The sign conventions for heat and work are crucial (Figure 5.3.5):

- Heat (q): Positive when heat is added to the system; negative when heat is removed from the system.
- Work (w): Positive when work is done on the system (compression); negative when work is done by the system (expansion).

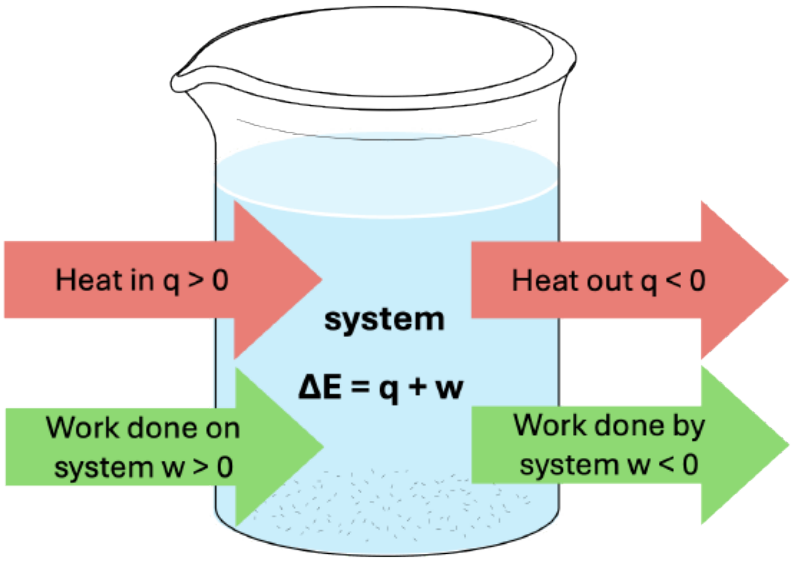


Figure 5.3.5: Heat entering the system and work being done on the system by the surroundings are positive quantities because they increase the internal energy of the system. Heating leaving the system and work being done by the system on the surroundings are negative quantities because they decrease the internal energy of the system.

Example 5.3.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔE) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 5.3.3.
B. Using Equation 5.3.4 calculate w from the values given. Substitute this value into Equation 5.3.3 to calculate ΔE.

Solution

A. From Equation 5.3.3, we know that ΔE = q + w. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B. Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 5.3.3,

$$w = -P_{\text{ext}}\Delta V = -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) = 284\ \text{J}$$

Thus

$$\begin{aligned}\Delta E &= q + w \\ &= -140\,J + 284\,J \\ &= 144\,J\end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 5.3.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔE) of the gas in joules?

Answer available at the end of this section.

Summary

In thermodynamics, the system refers to the specific part of the universe under study, while the surroundings encompass everything else.

A state function is a property that depends solely on the current state of the system, independent of the path taken to reach that state.

Internal energy (E) is a state function representing the total kinetic and potential energy of all particles in a system. Internal energy can be transferred as heat (q) or as work (w):

$$\Delta E_{sys} = q + w$$

The sign convention is important. Heat absorbed by the system is positive, while heat released by the system to the surroundings is negative. Similarly, work done on the system by the surroundings is positive, while work done by the system on the surroundings is negative. While internal energy is a state function and independent of how the system reached the energy, heat and work are not state functions.

Pressure-volume work occurs when the volume of a system changes against an external pressure. Under constant external pressure, it is calculated using $w = -P\Delta V$, where expansion ($\Delta V > 0$) means the system does work and loses energy, and compression ($\Delta V < 0$) means the surroundings do work on the system, increasing the internal energy of the system.

Energy is always conserved; it cannot be created or destroyed, only transformed from one form to another.

Glossary

expansion work (pressure-volume work)
: A type of mechanical work done as a system expands or contracts against external pressure.

first law of thermodynamics
: The internal energy of a system changes due to heat flow in or out of the system or work done on or by the system; also called the law of conservation of energy.

internal energy (E)
: The total of all possible kinds of energy present in a substance or substances.

state function
: A property depending only on the state of a system, and not the path taken to reach that state.

surroundings
: All matter other than the system being studied.

system
: The portion of matter undergoing a chemical or physical change being studied.

Answers

Exercise 5.3.1

$\Delta E = q + w \; q = +117J \text{ (heat to the gas)} \; w = -P\Delta V = -0.995atm(3.50L - 0.200L)\left(\frac{101.3J}{L \cdot atm}\right) = -333J \; \Delta E = 117J + -333J = -216J$

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5.4: Enthalpy

Learning Objectives

- Define the system and surroundings and explain heat flows in endothermic and exothermic processes.
- Define enthalpy as a state function related to internal energy, pressure, and volume.
- Interpret thermochemical equations and relate the magnitude and sign of Δ*H* to the reaction as written.
- Calculate the amount of heat transferred using a thermochemical equation and the quantity of reactant or product involved.

As discussed in the previous section, internal energy can be transferred as heat or work. Heat is the transfer of energy due to a temperature difference between the system and its surroundings. Work is the transfer of energy that does not require temperature differences. There are several types of work, but we will focus on pressure-volume work. Like heat, work describes energy in transit - it occurs only when energy is being transferred.

To further understand the relationship between heat (q) and the change in internal energy (ΔE), let's consider two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure.

Assuming pressure-volume work is the only kind of work possible for the system, we can substitute $w = -P\Delta V$ into the expression for change in internal energy, ($\Delta E = q + w$), giving:

$$\Delta E = q - P\Delta V \tag{5.4.1}$$

Constant Volume

In a closed, rigid container, the volume of the system does not change, so $\Delta V = 0$. At constant volume, no pressure-volume work can be done, and $w = -P\Delta V = 0$. Under these conditions, the amount of heat transferred between the system to the surroundings (denoted q_v for constant volume) is equal to the change in internal energy:

$$\underset{\text{constant volume}}{q_\text{v} = \Delta E} \tag{5.4.2}$$

Constant Pressure

Many chemical reactions are performed in open containers at approximately constant atmospheric pressure (about 1 atm). Heat under these conditions is given the symbol q_p to indicate constant pressure. Replacing q in Equation 5.4.1 by q_p and rearranging the equation gives:

$$\underset{\text{constant pressure}}{q_\text{p} = \Delta E + P\Delta V} \tag{5.4.3}$$

Thus, at constant pressure, heat is equal to the change in internal energy plus the pressure-volume work.

Because conditions of constant pressure are so common in chemistry, a new state function called enthalpy (H) is defined as the internal energy plus the product of pressure and volume.

$$H = E + PV$$

At constant pressure, the change in the enthalpy of a system is:

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + P\Delta V \tag{5.4.4}$$

$\Delta(PV)$ simplifies to $P\Delta V$ because pressure is constant. This means that, at constant pressure, the change in enthalpy is equal to the heat transferred: $\Delta H = q_p$. This matches our definition of enthalpy as the heat absorbed or released during a process at constant pressure. Importantly, under these conditions, ΔH can be determined by measuring only heat; work does not need to be

measured, which simplifies experimental procedures.

As with internal energy, it is the change in enthalpy that matters. Enthalpy, like internal energy, is a state function - its value depends only on the current state of the system, not the path taken to reach that state.

The Relationship between ΔH and ΔE

Enthalpy is often similar to internal energy, as many reactions involve little pressure-volume work. The following examples help illustrate when they are approximately equal and when they differ.

1. **Reactions involving only solids, liquids, or solutions**
   The volume does not change appreciably in these systems ($\Delta V \approx 0$), and so we can simplify Equation 5.4.4 to $\Delta H \approx \Delta E$.

2. **Reactions where the number of moles of gas does not change**
   If the total number of gas molecules is the same on both sides of the equation, then the volume remains reasonably constant ($\Delta V \approx 0$), so again $\Delta H \approx \Delta E$.

3. **Reactions where the number of moles of gas changes**
   In these cases $\Delta V \neq 0$, so ΔH and ΔE are not equal, however they still tend to be similar. To explore this idea, let's consider the conversion of oxygen gas to ozone at 298 K which involves the conversion of 3 moles of $O_2(g)$ to 2 moles of $O_3(g)$:

   $$3\,O_2\,(g) \rightarrow 2\,O_3\,(g)$$

   For this reaction, $\Delta H = 285.4kJ$ and $P\Delta V = -2.5kJ$. This is an endothermic reaction ($\Delta H > 0$) with a decrease in the number of moles of gas and so the system will decrease in volume ($\Delta V < 0$). Using these values we can calculate the change in internal energy of the system:

   $$\Delta E = \Delta H - P\Delta V = 285.4kJ - (-2.4kJ) = 287.9kJ$$

   We see that the change in internal energy ($\Delta E = 287.9kJ$) is greater than the enthalpy change ($\Delta H = 285.4kJ$), which is consistent with a decrease in volume as the surroundings did work on the system when its volume decreased. ΔE and ΔH are not identical, but they are very close, less than 1% different, and so even in cases where there is a change in volume ΔH is often a good approximation of ΔE.

From these examples we can see that in the majority of reactions most of the energy change appears as heat, so ΔH can be used as a good approximation of ΔE.

Example 5.4.1: The Relationship Between ΔH and ΔE

The combustion of graphite to produce carbon dioxide is described by the equation:

$$C_{(graphite,s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

At 298 K and 1.0 atm, ΔH = –393.5 kJ/mol of graphite for this reaction.

Would the change in internal energy (Δ*E*) be greater than, less than, or equal to the enthalpy change (Δ*H*)?

Strategy:

Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.

Solution

This reaction produces 1 mol of gas (CO_2) and consumes 1 mol of gas (O_2), so there is no net change in the number of gas molecules:

Δn = 1 – 1 = 0.

Because ΔV is approximately zero, the pressure-volume work term is negligible, and $\Delta E \approx \Delta H$.

Exothermic and Endothermic Processes

The sign of ΔH indicates whether heat is absorbed or released in a process. If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH is positive. Thus $\Delta H < 0$ for an exothermic reaction, and $\Delta H > 0$ for an endothermic reaction. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process.

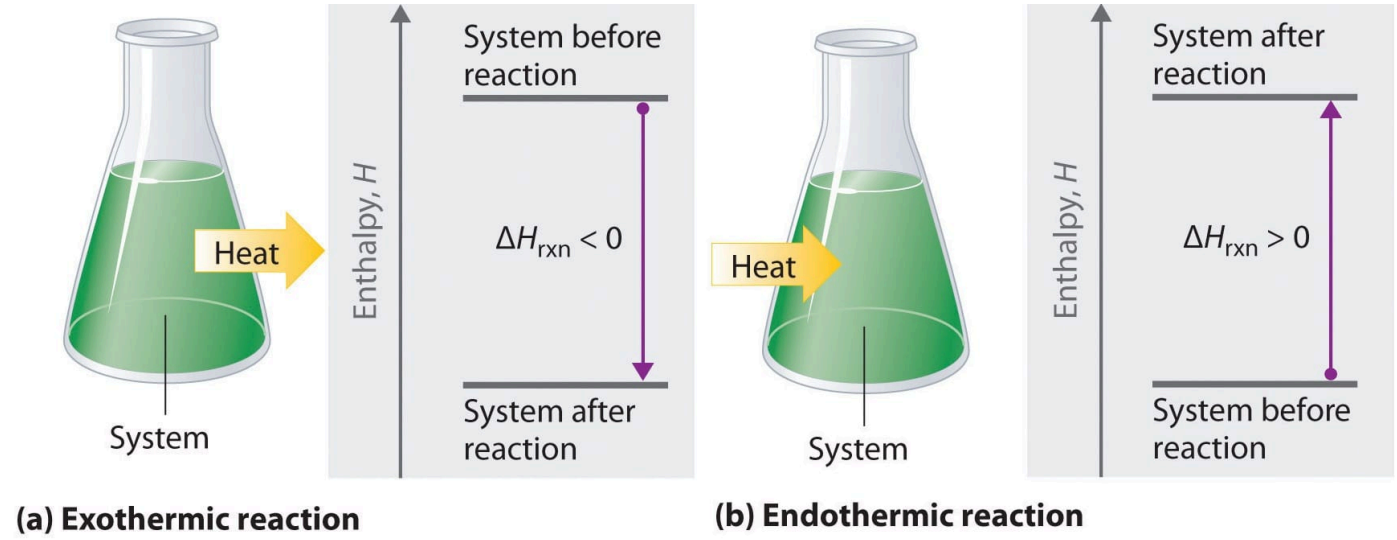


Figure 5.4.1: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH is negative, and the reaction is exothermic. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH is positive, and the reaction is endothermic.

Thermochemical Equations

Chemists use thermochemical equations to represent both the chemical change and the associated energy change of a reaction. In a thermochemical equation, the enthalpy change is written as a ΔH value following the balanced chemical equation. This ΔH value refers to the enthalpy change per mole of reactant and product in the reaction as written. How we manipulate ΔH values associated with chemical equations relate to the fact that ΔH is a state function and an extensive property. Extensive properties scale with the amount of a substance present. Mass, moles, and volume are all examples of extensive properties. The alternative is an intensive property, such as concentration or density, which do not scale with the amount of substance present.

Here are some key conventions to remember when dealing with ΔH values associated with chemical equations:

1. **The sign of ΔH indicates the direction of heat flow**
   A negative ΔH indicates an exothermic reaction where heat is released by the system (the chemical reaction) and transferred to the surroundings (often most noticeably to the solvent and container in which the reaction is occurring). A positive ΔH indicates an endothermic reaction where heat is absorbed by the system from the surroundings.

2. **If the direction of a chemical equation is reversed, the sign of ΔH also reverses**
   This relates to ΔH being a state function, the amount of heat released in one direction is exactly the same as the amount of heat absorbed in the reverse direction.

3. **If all coefficients in the balanced equation are multiplied or divided, the ΔH must be scaled by the same factor**
   This relates to ΔH being an extensive property. When the stoichiometry of the reaction is scaled by a factor, the enthalpy change must be scaled by the same factor. Let's use the reaction of hydrogen and oxygen to produce water as an example:

$$\mathrm{H_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{H_2O\,(l)} \quad \Delta H = -286 kJ/mol$$

This equation means that *if* 1 mol of $\mathrm{H_2\,(g)}$ was to react with 0.5 mol of $\mathrm{O_2\,(g)}$ to form 1 mol of $\mathrm{H_2O\,(l)}$, 286 kJ of heat is released. If we double the coefficients, we have doubled the stoichiometry of the reaction and twice as much of heat would be released per reaction as written:

$$\mathrm{2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l)} \quad \Delta H = 2 \times (-286 kJ/mol) = -572 kJ/mol$$

If we halve the stoichiometry we need to halve ΔH:

$$\mathrm{\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{4}\,O_2\,(g) \longrightarrow \tfrac{1}{2}\,H_2O\,(l)} \quad \Delta H = \frac{1}{2} \times (-286 kJ/mol) = -143 kJ/mol$$

The enthalpy change must always correspond the stoichiometric coefficients in the chemical equation as written.

4. **Units of ΔH, J/mol or kJ/mol, refer to the moles of reactants and products in the balanced chemical reaction**
   Using the example above we can see that the amount of energy generated per mole of hydrogen consumed is consistent as long as the per mole component of the ΔH unit takes the balanced stoichiometry of the reaction into account:
   $$\frac{-286 kJ}{1\ mol\ \mathrm{H_2\,(g)}} = \frac{-572 kJ}{2\ mol\ \mathrm{H_2\,(g)}} = \frac{-143 kJ}{\frac{1}{2}\ mol\ \mathrm{H_2\,(g)}}$$
5. **Stoichiometric coefficients in the balanced equation are unitless**
   These coefficients refer to the ratio of molecules of reactants and products in the reaction, not the actual amounts present. They do not carry units and should not be assigned "mol."
6. **The ΔH of a reaction depends on the physical states of the substances involved.**
   The ΔH for the production of water is different if the reaction produces liquid water ($\mathrm{H_2O\,(l)}$) or gas phase water ($\mathrm{H_2O\,(g)}$):
   $$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)} \quad \Delta H = -286 kJ/mol$$
   $$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)} \quad \Delta H = -242 kJ/mol$$
   Condensing water from gas to liquid releases additional heat energy because of the formation of stronger intermolecular forces, so the production of liquid water has a more negative ΔH. Because the physical state affects the enthalpy change, the physical states of all reactants and products must be specified in a thermochemical equation.

Example 5.4.2: Writing Thermochemical Equations

When 0.0500 mol of $\mathrm{HCl}(aq)$ reacts with 0.0500 mol of $\mathrm{NaOH}(aq)$ to form 0.0500 mol of $\mathrm{NaCl}(aq)$, 2.9 kJ of heat is released. What is Δ*H* for the following reaction?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), *q* = −2.9 kJ. The reactants are present in stoichiometric amounts (matching the 1:1 molar ratio in the balanced equation), and so the amount of acid (or base) may be used to calculate the molar enthalpy change. Since ΔH is an extensive property, it is proportional to the amount of substance reacted:

$$\Delta H = \frac{-2.9 kJ}{0.0500\ \mathrm{mol\ \ HCl}} = -58 kJ/mol$$

This gives the heat released per mole of HCl neutralized, consistent with the stoichiometry of the reaction.

The corresponding thermochemical equation is:

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

The heat released or absorbed in a chemical reaction depends on how much of each substance reacts. When calculating Δ*H*, it's

important to identify the limiting reactant, since it determines how much product forms—and how much energy is involved.

Exercise 5.4.1

When 1.34 g $\mathrm{Zn}(s)$ reacts with 60.0 mL of 0.750 M $\mathrm{HCl}(aq)$, 3.14 kJ of heat is produced. What is ΔH for the following reaction?

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

Answer available at the end of this section.

Example 5.4.3: Writing Thermochemical Equations

A gummy bear contains 2.67 g sucrose, $\mathrm{C_{12}H_{22}O_{11}}$. When it reacts with 7.19 g potassium chlorate, $\mathrm{KClO_3}$, 43.7 kJ of heat is produced. What is ΔH for the following reaction?

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

Solution

The limiting reactant must be identified: it determines how much heat is released.

Step 1: Calculate moles of each reactant:

$$\mathrm{(2.67\,g)\left(\frac{1\,mol}{342.3\,g}\right) = 0.00780\,mol\,C_{12}H_{22}O_{11}}$$

$$\mathrm{(7.19\,g)\left(\frac{1\,mol}{122.5\,g}\right) = 0.0587\,mol\,KClO_3}$$

Step 2: Use stoichiometry to find the limiting reactant

From the balanced equation, 1 mol of sucrose reacts with 8 mol of $\mathrm{KClO_3}$:

$$\mathrm{0.00780\,mol\,C_{12}H_{22}O_{11}\left(\frac{8\,mol\ KClO_3}{1\,mol\,C_{12}H_{22}O_{11}}\right) = 0.0624\,mol\ KClO_3\ (amount\ needed\ to\ react\ with\ all\ of\ sucrose)}$$

Since only 0.0587 mol of $\mathrm{KClO_3}$ are available, $\mathrm{KClO_3}$ is the limiting reactant and must be used to calculate the enthalpy change:

$$\mathrm{\Delta H = \frac{-43.7\,kJ}{0.0587\,molKClO_3} = -744\,kJ/mol}$$

This is the enthalpy change per mole of $\mathrm{KClO_3}$ consumed as written in the balanced equation. Since the equation involves 8 mol $\mathrm{KClO_3}$, the total ΔH is:

$$\mathrm{-744\,kJ/mol \times 8 = -5960\,kJ/mol}$$

The thermochemical equation is:

$$\mathrm{C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl \quad \Delta H = -5960\,kJ/mol}$$

Exercise 5.4.2

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $\mathrm{FeCl_2\,(s)}$ and 8.60 kJ of heat is produced. What is ΔH for the following reaction?

$$\mathrm{Fe\,(s) + Cl_2\,(g) \ \rightarrow FeCl_2\,(s)}$$

Answer available at the end of this section.

Summary

- At constant volume, no pressure-volume work is done, so the heat transferred equals the change in internal energy: $q_v = \Delta E$
- At constant pressure, the heat transferred equals the change in enthalpy: $q_p = \Delta H$
  - Enthalpy (H) is a state function defined as: H = E + PV
  - Therefore, $\Delta H = \Delta E + P\Delta V$ at constant pressure
- In many reactions—especially those involving only solids, liquids, or solutions—the volume change is negligible, so: $\Delta H \approx \Delta E$
  - Even when gas is involved, if pressure-volume work is small, this approximation often remains valid.
- The sign of ΔH indicates the direction of heat flow:
  - $\Delta H < 0$: Exothermic (heat is released to the surroundings)
  - $\Delta H > 0$: Endothermic (heat is absorbed from the surroundings)
- A thermochemical equation includes both the balanced chemical reaction and the enthalpy change (ΔH). Key points to remember:
  - ΔH is associated with the reaction as written.
  - If the reaction is reversed, the sign of ΔH is reversed.
  - If the reaction is multiplied or divided by a factor, ΔH is scaled by the same factor.
  - The physical states of reactants and products must be specified, as they affect the enthalpy change.
  - The magnitude of ΔH refers to the amount of heat transferred following one mole of the reaction as written.
- The heat transferred in a reaction depends on the amount of limiting reactant, since it determines how much product forms and, therefore, how much energy is released or absorbed.

Glossary

endothermic
: Describes a chemical reaction or physical change that absorbs heat.

enthalpy (*H*)
: The sum of a system's internal energy and the mathematical product of its pressure and volume.

enthalpy change (ΔH)
: Heat released or absorbed by a system under constant pressure during a chemical or physical process.

exothermic
: Describes a chemical reaction or physical change that releases heat.

Answers

Exercise 5.4.1

Step 1: Calculate the moles of each reactant:

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

$$1.34g\ Zn\left(\frac{mol}{65.38g}\right) = 0.0205\ mol\ Zn$$

$$0.750\ \frac{mol}{L} HCl(0.0600L) = 0.0450\ mol\ HCl$$

According to the balanced chemical equation, 2 mol of HCl are required for every 1 mol of Zn. The amount of HCl present is more than twice the amount of Zn, so Zn is the limiting reactant.

Step 2: Use the limiting reactant to determine ΔH:

$$\Delta H = \frac{-3.14kJ}{0.0205mol} = -153kJ/mol$$

This is the enthalpy change for the reaction as written, per mole of Zn reacted.

Exercise 5.4.2

Since the amount of product is given, we can find the enthalpy change without considering the limiting reactant.

Step 1: Convert mass of product to moles:

$$3.22\ g\ \mathrm{FeCl_2\,(s)}\left(\frac{mol}{126.75\ g}\right) = 0.0254\,mol$$

Step 2: Calculate ΔH per mole of product formed:

$$\Delta H = \frac{-8.60\,\text{kJ}}{0.0254\,mol} = -339\,\text{kJ/mol}$$

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5.5: Calorimetry

Learning Objectives

- Explain how calorimetry demonstrates the law of conservation of energy.
- Describe the relationship between heat (q), temperature change (ΔT), and heat capacity (C, specific and molar).
- Analyze calorimetry data to calculate heat transferred (q), temperature change (ΔT), heat capacity (C), and the change in enthalpy (ΔH) or internal energy (ΔE).

Thermal energy cannot be measured directly, but the temperature change caused by heat transfer can be. Calorimetry refers to a set of techniques used to measure energy changes in chemical processes using devices called calorimeters. For these measurements to be meaningful, the temperature change observed must be related to the amount of heat absorbed or released by the system. We begin this section by exploring how heat affects temperature.

Heat Capacity

We've seen that the temperature of an object changes when it absorbs or loses thermal energy. The temperature change depends on both the amount of heat transferred (q) and the object's heat capacity (C), which is the amount of energy required to raise the temperature of the object by 1 °C. Units are joules per degree Celsius (J/°C):

$$\text{Heat Capacity (C)} = \frac{q}{\Delta T}$$

where q is the amount of heat (in joules), and ΔT is $T_{final} - T_{initial}$. Since the size of one Kelvin is equal to one degree Celsius, ΔT is the same whether in K or °C, as long as you don't mix the units within a single calculation.

The heat capacity of an object depends on both its mass and its composition. For example, doubling the mass of an object doubles its heat capacity. Because of this, heat capacity is often reported per gram or per mole of substance.

The **molar heat capacity (C_m)** is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_m for molar heat capacity are thus J/(mol °C). We can relate the quantity of a substance in moles (n), the amount of heat transferred (q), its molar heat (C_m), and the temperature change (ΔT):

$$q = nC_m\Delta T \tag{5.5.1}$$

The **specific heat capacity (C)** is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g°C). We can use the specific heat capacity to relate the mass of a substance (m), the amount of heat transferred (q), its specific heat (c), and the temperature change (ΔT):

$$q = mc\Delta T \tag{5.5.2}$$

The specific heat capacities of some common substances are given in Table 5.5.1. Most solids have specific heat values below 1 J/(g·°C), and most liquids are around 2 J/(g·°C). Water is a major exception: the specific heat of ice is about twice that of most solids, and the specific heat of liquid water (4.18 J/(g·°C)) is among the highest known.

Table 5.5.1: Specific Heats of Selected Substances at 25°C

Compound	Specific Heat [J/(g°C)]	Compound	Specific Heat [J/(g°C)]
$H_2O(s)$ (-10°C)	2.05	Al(s)	0.897
$H_2O(l)$	4.18	Fe(s)	0.449
$H_2O(g)$	2.062	Cu(s)	0.385
CH_3OH (methanol)	2.531	Au(s)	0.129

Compound	Specific Heat [J/(g°C)]	Compound	Specific Heat [J/(g°C)]
CH_3CH_2OH (ethanol)	2.438	Hg(l)	0.140
n-$C_6H_{14}(s)$ (n-hexane)	2.270	NaCl(s)	0.864
$C_6H_6(s)$ (benzene)	1.741	MgO(s)	0.918
$C(s)$ (graphite)	0.709	SiO_2(s) (quartz)	0.742
$C(s)$ (diamond)	0.509	$CaCO_3$(s) (calcite)	0.915

Water's unusually high specific heat has important implications for life on Earth. For a 1 °C temperature change, a given mass of water stores or releases more than five times as much heat as the same mass of granite or limestone. This is why coastal regions have milder climates than inland areas: the ocean absorbs heat in summer and releases it slowly in winter. It's also why swimming pools and waterbeds are heated - large amounts of energy are needed to raise and maintain a comfortable temperature. Because the human body is approximately 70% water by mass, it resists temperature change. This helps regulate our internal body temperature without requiring overly fine control.

Example 5.5.1: Solar Heating

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0 °C. During the day, the water temperature rises to 38.0 °C as it circulates through the water wall. How much energy has been stored in the water? The density of water at 22.0 °C is 0.998 g/mL, and specific heat capacity is 4.18 J/(g°C).



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0 °C to obtain the mass of water that corresponds to 400 L of water. Then compute ΔT for the water.
B. Determine the amount of heat absorbed by substituting values for mass, specific heat capacity, and ΔT into Equation 5.5.2.

Solution:

A The mass of water is

$$\text{mass of } H_2O = 400 \cancel{L}\left(\frac{1000 \cancel{mL}}{1 \cancel{L}}\right)\left(\frac{0.998\ g}{1 \cancel{mL}}\right)$$
$$= 3.99 \times 10^5 g\ H_2O$$

The temperature change (ΔT) is

$$38.0^oC - 22.0^oC = +16.0^oC.$$

B From Table 5.5.1, the specific heat of water is 4.18 J/(g°C). From Equation 5.5.2, the heat absorbed by the water is thus

$$q = mc\Delta T$$
$$= \left(3.99 \times 10^5 \cancel{g}\right)\left(\frac{4.18\ J}{\cancel{g} \cdot \cancel{^oC}}\right)\left(16.0\ \cancel{^oC}\right)$$
$$= 2.67 \times 10^7\ J = 2.67 \times 10^4\ kJ$$

Both q and ΔT are positive, consistent with the water absorbing energy.

Exercise 5.5.1: Solar Heating

Some solar heating systems circulate air over a bed of rocks to absorb thermal energy from the sun. If a house uses a system with 2500 kg of sandstone rocks, what amount of energy is stored if their temperature increases from 20.0 °C to 34.5 °C during the day? Assume the specific heat of sandstone is approximately the same as that of quartz (SiO_2, 0.742 J/(g·°C).

Answer available at the end of this section.

Principle of Calorimetry

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until both reach the same final temperature. According to the law of conservation of energy, the total energy remains constant during this process:

$$q_{cold} + q_{hot} = 0 \tag{5.5.3}$$

This means that the amount of heat lost by the warmer object is equal to the amount of heat gained by the cooler object. Because heat flows in opposite directions for each, the signs of their q values are also opposite:

$$q_{cold} = -q_{hot} \tag{5.5.4}$$

We can use this relationship to calculate the final temperature when two substances at different initial temperatures are brought into contact, as long as we know their mass and specific heat capacity.

For example, if a hot metal block is placed into cool water, heat flows from the metal to the water (Figure 5.5.1). The heat lost by the metal equals the heat gained by the water. This principle is used in calorimetry to determine unknown temperatures, specific heats, or other thermal properties. A calorimeter is a thermally insulated container that limits heat exchanged between its contents and the wider surroundings to facilitate calorimetry experiments. Calorimeters will have their own heat capacities that need to be measured, however these are often negligible in comparison to their contents and can sometimes be ignored in calculations.

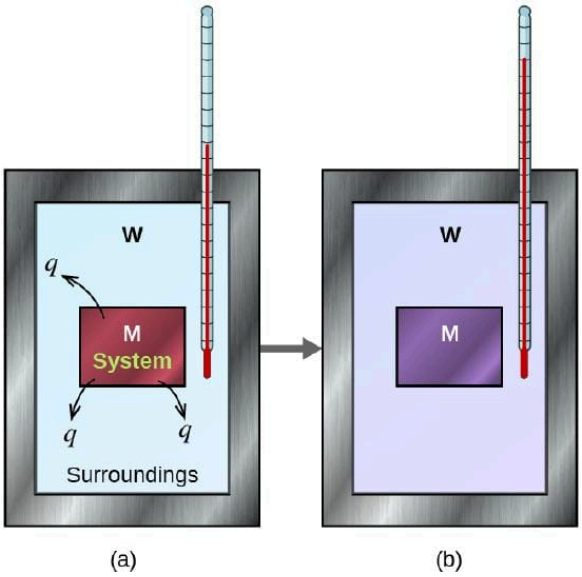


Figure 5.5.1: Heat flows from the hot metal (M) to the cooler water (W) in part (a), until they have the same final temperature in part (b). At this point, thermal equilibrium is achieved.

Example 5.5.2: Thermal Equilibration of Copper and Water

If a 30.0 g piece of copper pipe (c = 0.385 J/(g°C)) at 80.0 °C is placed in 100.0 g of water (c = 4.18 J/(g°C)) at 27.0 °C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass, initial temperature, and specific heat capacity of two objects

Asked for: final temperature

Strategy: The heat lost by the metal must be gained by the water:

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

The final temperature reached by the metal and water must be the same.

Solution

The heat of the metal and water can be written in terms of the specific heat capacity, mass, and temperature change:

$$\begin{aligned} q_{\text{metal}} &= -q_{\text{water}} \\ c_{\text{metal}}(m_{\text{metal}})(T_f - T_i) &= -c_{\text{water}}(m_{\text{water}})(T_f - T_i) \\ (0.385\frac{J}{g°C})(30.0g)(T_f - 80.0°C) &= -(4.18\frac{J}{g°C})(100.0g)(T_f - 27.0°C) \\ 11.55\frac{J}{°C}T_f - 924J &= -418\frac{J}{°C}T_f + 11286J \\ 429.55\frac{J}{°C}T_f &= 12210J \\ T_f &= 28.4°C \end{aligned}$$

It is expected that the water will increase in temperature since the added copper pipe was hotter than the water. However, the temperature increase is small because the water has both a much greater mass (three times more) and a much higher specific heat capacity (over 10 times greater) than copper.

Exercise 5.5.2: Thermal Equilibration of Gold and Water

If a 14.0 g chunk of gold (c= 0.129 J/(g°C)) at 20.0°C is dropped into 25.0 g of water (c = 4.18 J/(g°C)) at 80.0 °C, what is the final temperature if no heat is transferred to the surroundings?

Answer available at the end of this section.

Exercise 5.5.3: Thermal Equilibration of Aluminum and Water

A 28.0 g chunk of aluminum (c = 0.897 J/(g°C)) is dropped into 100.0 g of water (c = 4.18 J/(g°C)) with an initial temperature of 20.0 °C. If the final temperature of the water is 24.0 °C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer available at the end of this section.

Calorimetry of Chemical Reactions

Reactions carried out in a calorimeter can cause a temperature change in the contents of the calorimeter, which reflect the energy change of the reaction. The purpose of a calorimeter is to isolate the reaction from the wider surroundings so these energy flows can be properly measured using temperature changes. Within the calorimeter, the chemical reaction is the system and the calorimeter and its contents are the surroundings. The amount of heat absorbed or released by the system is equal in magnitude and opposite in sign to the heat exchanged by the surroundings:

$$q_{system} = -q_{surroundings}$$

- If the reaction releases heat ($q_{system} < 0$), the calorimeter absorbs heat ($q_{surroundings} > 0$), and its temperature rises.
- If the reaction absorbs heat ($q_{system} > 0$), the calorimeter loses heat ($q_{surroundings} < 0$), and its temperature falls.

The heat absorbed or released by the calorimeter ($q_{surroundings}$) includes the physical interior of the calorimeter ($q_{calorimeter}$) and any solvents ($q_{solvent}$) present in solution-based reactions:

$$q_{surroundings} = q_{calorimeter} + q_{solvent}$$

In practical terms, the heat exchanged by the calorimeter is often small compared to the heat exchanged by the solvent ($q_{solvent} > q_{calorimeter}$) and so we often assume $q_{calorimeter}$ is negligible and use the following relationship in calculations:

$$q_{system} = -q_{surroundings}$$
$$q_{system} = -(q_{calorimeter} + q_{solvent})$$
$$q_{system} \approx -q_{solvent}$$

With this relationship we can use the heat capacity of the solvent, the amount of solvent present, and the measured change in temperature to calculate how much energy was transferred by the reaction. Be sure to use consistent units for the amount of solvent (mass or moles) with the heat capacity used.

$$q_{system} \approx -n_{solvent} C_{solvent} \Delta T_{solvent}$$

Once we know the total heat transferred by a chemical reaction, we can calculate the heat released or absorbed per gram or per mole of reactant, based on the amounts of substances involved.

Constant-Pressure Calorimetry

A constant-pressure calorimeter is one of the simplest types of calorimeters. It usually consists of an insulated container, a thermometer, a stirrer, and a loosely fitting lid. A common example is the coffee-cup calorimeter, shown in Figure 5.5.2.

In this type of calorimeter, the pressure remains constant because the system is open to the atmosphere. This allows us to directly

measure the enthalpy change of the reaction (ΔH_{rxn}), which is the heat transferred at constant pressure ($q_p = q_{rxn} = q_{system}$). As discussed above, the heat released or absorbed by the reaction is equal in magnitude and opposite in sign to the heat absorbed or released by the calorimeter and its contents.

$$\Delta H_{rxn} = q_{system} = -q_{surroundings} \approx -q_{solvent} \tag{5.5.5}$$

The use of a constant-pressure calorimeter is illustrated in Example 5.5.3.

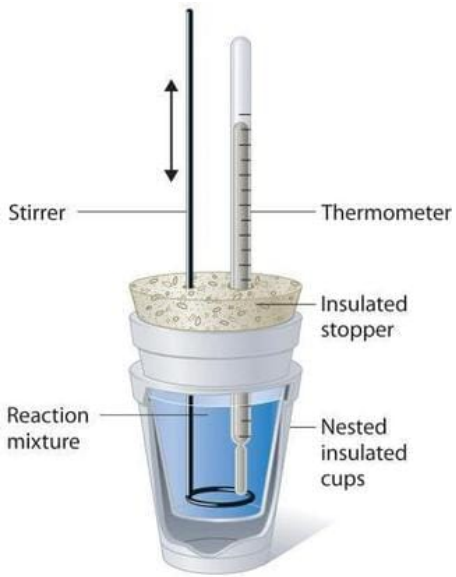


Figure 5.5.2: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Example 5.5.3: ΔH for Dissolution of Potassium Hydroxide

When 5.03 g of solid potassium hydroxide is dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the solution increases from 23.0 °C to 34.7 °C. What is ΔH (in kilojoules per mole) for the dissolution of KOH in water?

Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat capacity of the solution is the same as the specific heat capacity of pure water (4.184 J/(g°C)). The density of the water is 0.9969 g/cm^3.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH

Strategy:

A. Calculate the mass of the solution from the volume and density of water and the mass of KOH. Calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution using the specific heat, mass, and temperature change of the solution.
C. Use the molar mass of KOH to calculate ΔH.

Solution:

A To calculate ΔH, we must first determine the amount of heat released in the calorimetry experiment.

$-q_{sys} = q_{surr} = q_{sol}$

To calculate the heat of the surroundings, we need the total mass of the solution, which includes both the mass of the water and the mass of the KOH.

The mass of the solution is

$$\left(100.0\ \cancel{mL}\ \mathrm{H_2O}\right)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ \mathrm{KOH} = 104.72\ g$$

The temperature change is

$$(34.7\,^oC - 23.0\,^oC) = +11.7\,^oC.$$

B We assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$\begin{aligned} q_{sol} &= mc\Delta T \\ &= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)\left(11.7\ \cancel{^oC}\right) \\ &= 5130\ J = 5.13\ kJ \end{aligned}$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water.

$$q_{rxn} = -q_{sol} = -5.13\,kJ$$

This experiment shows that dissolving 5.03 g of KOH in water releases 5.13 kJ of heat. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH, i.e., the heat released when dissolving 1 mol of KOH:

$$\begin{aligned} \Delta H &= \left(\frac{-5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) \\ &= -57.2\ kJ/mol \end{aligned}$$

Because energy is an extensive property, it depends on the amount of substance, we report enthalpy changes per mole of reactant so the value can be applied to other quantities or used in thermochemical equations.

Exercise 5.5.4: ΔH for Dissolution of Ammonium Bromide

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7 °C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 5.5.3, find ΔH for the dissolution of $\mathrm{NH_4Br}$ (in kilojoules per mole).

Answer available at the end of this section.

Example 5.5.4 Heat Produced by an Exothermic Reaction

When 50.0 mL of 1.00 M $\mathrm{HCl}(aq)$ and 50.0 mL of 1.00 M $\mathrm{NaOH}(aq)$, both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. Assume that the calorimeter absorbs a negligible amount of heat and that the specific heat of the solution is the same as the specific heat of pure water (4.184 J/(g°C)). The density of the solution is 1.0 g/mL.

What is ΔH_{rxn} in kJ/mol?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)}$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. Before the reaction begins, the combined solution has a total volume of 100.0 mL and an initial temperature of 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat released by the neutralization reaction is absorbed by the solution, raising its temperature. Therefore:

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

(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 the outside environment.)

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

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

$q_{solution} = (4.184 J/g\,°C)(100.0 mL)(1.0 g/mL)(28.9\,°C - 22.0\,°C) = 2887 J = 2.9 kJ$

$q_{reaction} = -q_{solution} = -2.9 kJ$

Finally, we divide by the number of moles of reaction that occurred. The balanced equation shows that 1 mol of HCl reacts with 1 mol of NaOH. Since the reactants are present in equal amounts:

$\mathrm{mol\ HCl} = \mathrm{mol\ NaOH} = 1.00 \frac{mol}{L}(0.0500 L) = 0.0500 mol$

$\Delta H = \frac{-2.89 kJ}{0.0500 mol} = -58 kJ/mol$

This value represents the enthalpy change for the neutralization of one mole of a strong acid with a strong base.

Chemistry in Everyday Life: Thermochemistry of Hand Warmers

On a cold day, you might use a hand warmer to keep your hands warm while working or playing outside. A common reusable hand warmer contains a supersaturated solution of sodium acetate ($\mathrm{NaCH_3COO}$) and a small metal disk. Bending the disk triggers nucleation sites, which cause the sodium acetate to rapidly crystallize from the solution.

The process:

$$\mathrm{NaCH_3COO\,(aq) \rightarrow NaCH_3COO\,(s)}$$

is exothermic. That heat is transferred to your hands, providing warmth (at least temporarily!). When the hand warmer is reheated, the sodium acetate redissolves, and the device can be used again.



Exercise 5.5.5 Heat Flow in an Instant Ice Pack

When solid ammonium nitrate (NH_4NO_3) dissolves in water, the solution becomes cold. This is the principle behind an instant cold pack.

In a calorimetry experiment, 3.21 g of solid NH_4NO_3 is dissolved in 50.0 g of water at 24.9 °C in a calorimeter. After the salt dissolves, the final temperature of the solution is 20.3 °C.

Assume:

- The calorimeter absorbs a negligible amount of heat.
- The specific heat of the solution is the same as the specific heat of pure water (4.184 J/(g°C)).
- The density of the solution is 1.0 g/mL.

What is ΔH (in kilojoules per mole) for the dissolution of NH_4NO_3 in water?



An instant cold pack contains ammonium nitrate and water in separate compartments. When the inner pouch is broken, the ammonium nitrate dissolves and absorbs heat, cooling the pack.

Answer available at the end of this section.

Constant-Volume Calorimetry

Constant-pressure calorimeters are not well suited for reactions involving gases, such as combustion reactions, because gases often produce large pressure and volume changes that are difficult to contain or measure accurately in an open system. For these, a constant-volume calorimeter, such as a bomb calorimeter, is used (Figure 5.5.3).

In a bomb calorimeter, the reactant is placed in a steel cup inside a sealed steel container with a fixed volume (called the “bomb”). The bomb is filled with excess oxygen gas, sealed, and placed inside an insulated container holding a known mass of water.

Because combustion reactions are typically exothermic, they release heat, which raises the temperature of the surrounding water bath and the calorimeter. If the heat capacity of the bomb and the mass of water are known, the heat released by the reaction can be calculated.

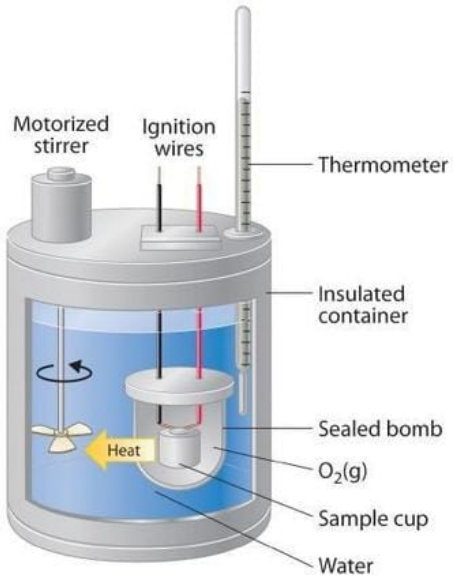


Figure 5.5.3: A Bomb Calorimeter. The reaction is triggered by passing an electric current through a wire that ignites the sample. Since the volume is fixed, the heat measured corresponds to the change in internal energy of the reaction, not the enthalpy.

Because the volume of the system is constant (the bomb cannot expand or contract), the pressure changes during the reaction, but no pressure-volume work is done. As a result, the heat released is equal to the change in internal energy (ΔE):

$$q_v = \Delta E$$

This contrasts with constant-pressure calorimetry, where the heat measured corresponds to (ΔH). As discussed earlier, ΔE and ΔH are often similar, especially when the number of moles of gas doesn't change much.

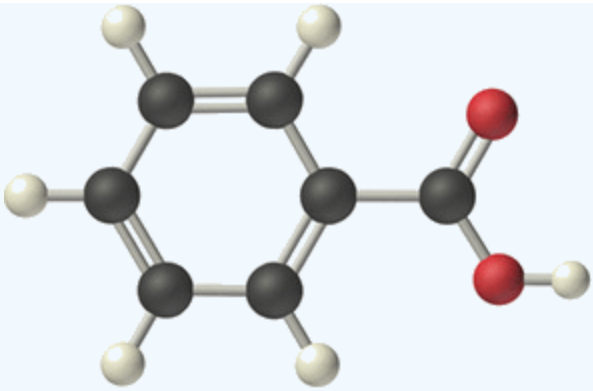
Before using a bomb calorimeter to measure unknown heats of combustion, we must determine the heat capacity of the calorimeter setup (including the water and bomb). To do this, a carefully weighed mass of a compound with a known heat of combustion is burned. A common standard is benzoic acid ($\mathrm{C_5H_5COOH}$), a pure, stable crystalline solid. The combustion of benzoic acid releases 26.38 kJ/g. Using the mass of benzoic acid burned and the temperature increase of the calorimeter, we can calculate the heat capacity of the bomb, C_{cal}.

Example 5.5.5: Combustion of Glucose

A bomb calorimeter is first calibrated using 0.579 g of benzoic acid. The combustion of this sample causes the temperature of the calorimeter to increase by 2.08 °C.

After calibration, the calorimeter is recharged with 1.732 g of glucose ($\mathrm{C_6H_{12}O_6}$) and excess oxygen. When the glucose is ignited, the temperature of the calorimeter increases by 3.64 °C.

Given that the combustion of benzoic acid releases 26.38 kJ/g, calculate the change in internal energy (ΔE) for the combustion of glucose in kJ/mol.



Benzoic acid

Given: mass and ΔT for combustion of benzoic acid and glucose

Asked for: Δ*E* for combustion of glucose (in kJ/mol)

Strategy:

A. Use the benzoic acid data to find the heat capacity of the calorimeter.
B. Use that heat capacity to calculate the heat released in the combustion of glucose.
C. Find Δ*E* in kJ/mol by dividing by the number of moles of glucose.

Solution:

A. Calculate heat released by benzoic acid:

$q_{rxn} = (0.579g)(-26.38kJ/g) = -15.3kJ$

Note: since heat is released, the value is negative.

Use this value to find the heat capacity of the calorimeter:

$q_{rxn} = -q_{cal} = -C_{cal}\Delta T \; C_{cal} = \frac{-q_{cal}}{\Delta T} = \frac{-(-15.3kJ)}{2.08°C} = 7.34kJ/\,°C$

B. Use the heat capacity from A to find the heat released in the combustion of glucose:

$q_{rxn} = -q_{cal} = -C_{cal}\Delta T = -7.34kJ/\,°C(3.64\,°C) = -26.7kJ$

C. Calculate the moles of glucose:

$\text{mol glucose} = \frac{1.732g}{180.16g/mol} = 0.00961mol$

Convert to kJ/mol

$\Delta E = \frac{-26.7kJ}{0.00961mol} = -2780 \;\; kJ/mol$

Exercise 5.5.6: Combustion of Methlhydrazine

Methylhydrazine is used as a rocket fuel.

To find the heat associated with this fuel, a bomb calorimeter is first calibrated using 2.123 g of benzoic acid. The combustion of this sample causes the temperature of the calorimeter to increase by 4.75 °C.

After calibration, the calorimeter is recharged with 1.932 g of methylhydrazine (CH_3NHNH_2) and excess oxygen. When the methylhydrazine is ignited, the temperature of the calorimeter increases by 4.64 °C.

Given that the combustion of benzoic acid releases 26.38 kJ/g, calculate the change in internal energy (ΔE) for the combustion of methylhydrazine in kJ/mol.



Methylhydrazine

Answer available at the end of this section.

Chemistry in Everyday Life: Measuring Nutritional Calories

You've probably seen energy listed on food labels in Calories. But what exactly is a Calorie?

In science, 1 calorie (cal) is defined as the amount of energy needed to raise the temperature of 1 gram of water by 1 °C. One Calorie (with a capital C), also known as a nutritional Calorie, is equal to 1000 cal, or 1 kilocalorie (kcal). This is about the amount of energy needed to raise the temperature of 1 kg of water by 1 °C.

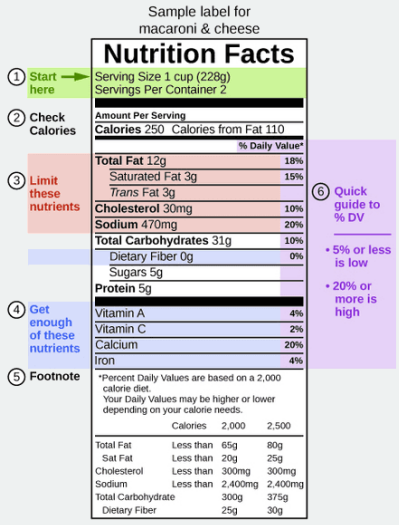
The energy content of food comes from the macronutrients: carbohydrates, proteins, and fats. On average:

- Carbohydrates provide 4 Calories per gram
- Proteins provide 4 Calories per gram
- Fats provide 9 Calories per gram

These values are reflected on nutrition labels (Figure 5.5.4).



(a)



(b)

Figure 5.5.4: (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. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), a 1-cup serving of macaroni and cheese contains 5 g protein, 31 g carbohydrates and 12 g fat.

We can estimate the total energy using average values for each macronutrient:
(5 g protein × 4 Cal/g) + (31 g carbs × 4 Cal/g) + (12 g fat × 9 Cal/g) = 252 Cal

This aligns closely with the 250 Calories shown on the label.

Where do these numbers come from?

Originally, the caloric content of food was measured using bomb calorimetry: the food is dried, ground, and formed into a pellet, which is then combusted in a bomb calorimeter to measure the energy released.

Today, most nutrition labels use the Atwater system, which assigns average energy values to each macronutrient based on calorimetry data from real foods. For example, the energy from carbohydrates is adjusted to subtract fiber (which isn't digested and doesn't contribute Calories). The final caloric value is calculated from the amounts of each nutrient in the food.

Summary

Calorimetry is a set of techniques used to measure heat changes during chemical processes. It uses devices called calorimeters, which detect temperature changes during a chemical reaction. The size of the temperature change depends on both the amount of heat transferred and the heat capacity of the system.

- Heat capacity (C) is the energy needed to raise the temperature of an object by 1 °C (units: J/°C).
- Specific heat capacity (c) is the energy needed to raise the temperature of 1 g of a substance by 1 °C (units: J/g·°C).
- Molar heat capacity (C) is the energy needed to raise the temperature of 1 mol of a substance by 1 °C (units: J/mol·°C).

Water has a very high specific heat, which helps regulate temperature in the environment and in living organisms.

According to the law of conservation of energy, any heat released or absorbed by a system must be absorbed or released by the surroundings.

Heat measurements are typically made using:

- Constant-pressure calorimetry: measures heat at constant pressure and gives the enthalpy change, ΔH
  - $q_p = \Delta H$
- Constant-volume (bomb) calorimetry: used for reactions involving gases, such as combustion, and gives the change in internal energy, ΔE
  - $q_v = \Delta E$

Glossary

bomb calorimeter
: A 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.

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.

calorimetry
: Process of measuring the amount of heat involved in a chemical or physical process.

constant-pressure calorimeter
: Calorimeter in which the pressure remains constant because the system is open to the atmosphere.

constant-volume calorimeter
: Calorimeter in which the volume remains constant, creating a closed system often used for non-gases.

heat capacity (C)
: The 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).

molar heat capacity (C_m)
: The amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; measured in J/(mol °C).

specific heat capacity (c)
: The 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).

Answers

Exercise 5.5.1: Solar Heating

$$\begin{aligned} q &= mc\Delta T \\ &= \left(2500 \cancel{kg}\right)\left(\frac{1000\,\cancel{g}}{\cancel{kg}}\right)\left(\frac{0.742\ J}{\cancel{g}\cdot\cancel{^oC}}\right)\left((34.5-20.0)\ \cancel{^oC}\right) \\ &= 2.68\times10^7\ J = 2.68\times10^4\ kJ \end{aligned}$$

Even though the mass of sandstone is more than six times the mass of the water in Example 5.5.1, the thermal energy stored is nearly the same due to water's much higher specific heat capacity.

Exercise 5.5.2: Thermal Equilibration of Gold and Water

$$\begin{aligned} q_{\text{metal}} &= -q_{\text{water}} \\ c_{\text{metal}}(m_{\text{metal}})(T_f - T_i) &= -c_{\text{water}}(m_{\text{water}})(T_f - T_i) \\ (0.129\frac{J}{g^\circ C})(14.0g)(T_f - 20.0^\circ C) &= -(4.18\frac{J}{g^\circ C})(25.0g)(T_f - 80.0^\circ C) \\ 1.806\frac{J}{^\circ C}T_f - 36.12J &= -104.5\frac{J}{^\circ C}T_f + 8360J \\ 106.306\frac{J}{^\circ C}T_f &= 8396.12J \\ T_f &= 79.0^\circ C \end{aligned}$$

Exercise 5.5.3: Thermal Equilibration of Aluminum and Water

$$\begin{aligned} q_{\text{metal}} &= -q_{\text{water}} \\ c_{\text{metal}}(m_{\text{metal}})(T_f - T_i) &= -c_{\text{water}}(m_{\text{water}})(T_f - T_i) \\ (0.897\frac{J}{g^\circ C})(28.0g)(24.0^\circ C - T_i) &= -(4.18\frac{J}{g^\circ C})(100.0g)(24.0^\circ C - 20.0^\circ C) \\ 602.784J - 25.116\frac{J}{^\circ C}T_i &= -1672J \\ T_i &= 90.6^\circ C \end{aligned}$$

Exercise 5.5.4: ΔH for Dissolution of Ammonium Bromide

$$\left(50.0\ \cancel{mL}\ \text{H}_2\text{O}\right)\left(0.9969\ g/\cancel{mL}\right) + 3.14\ g\ \text{KOH} = 52.985\ g$$

$$\begin{aligned} q_{rxn} = -q_{water} &= -mc\Delta T \\ &= -\left(52.985\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)(-2.4\ ^oC) \\ &= 532J \end{aligned}$$

$$3.14g\left(\frac{mol}{97.94g}\right) = 0.0321mol$$

$$\Delta H = \frac{532J}{0.0321mol} = 16594\ J/mol = 16.6\ kJ/mol$$

Exercise 5.5.5 Heat Flow in an Instant Ice Pack

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

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

$$\begin{aligned} q_{solution} &= mc\Delta T \\ &= \left(53.21\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)(20.3\ ^oC - 24.9\ ^oC) \\ &= -1024\ J = -1.02\ kJ \end{aligned}$$

$$q_{reaction} = -q_{solution} = +1.02kJ$$

$$\begin{aligned} \Delta H_{soln} &= \left(\frac{1.02\ kJ}{3.21\ \cancel{g}}\right)\left(\frac{80.04\ \cancel{g}}{1\ mol}\right) \\ &= +25.5\ kJ/mol \end{aligned}$$

This positive value confirms that the dissolution of ammonium nitrate is endothermic: it absorbs heat from the surroundings, which causes the cold pack to feel cold.

Exercise 5.5.6: Combustion of Methlhydrazine

A. Calculate heat released by benzoic acid:

$q_{rxn} = (2.123g)(-26.38kJ/g) = -56.0kJ$

Note: since heat is released, the value is negative.

Use this value to find the heat capacity of the calorimeter:

$q_{rxn} = -q_{cal} = -C_{cal}\Delta T\ C_{cal} = \frac{-q_{cal}}{\Delta T} = \frac{-(-56.0kJ)}{4.75°C} = 11.8kJ/\ °C$

B. Use the heat capacity from A to find the heat released in the combustion of methylhydrazine:

$q_{rxn} = -q_{cal} = -C_{cal}\Delta T = -11.8kJ/\ °C(4.64\ °C) = -54.7kJ$

C. Calculate the moles of methylhydrazine:

$\text{mol methylhydrazine} = \frac{1.932g}{46.07g/mol} = 0.00419mol$

Convert to kJ/mol

$\Delta E = \frac{-54.7kJ}{0.00419mol} = -1300\ \ kJ/mol$

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5.6: Hess's Law

Learning Objectives

- Use Hess's Law to calculate the enthalpy change of a reaction by combining equations with known enthalpy changes.
- Explain how reversing or scaling chemical equations affects the enthalpy change, and account for physical states when applying Hess's Law.

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other reactions with known enthalpy changes. Some reactions are difficult, if not impossible, to study directly. Even when a reaction is easy to measure, it's often useful to calculate the enthalpy change from other known reactions.

Hess's Law states that if a process occurs in multiple steps, the total enthalpy change is the sum of the enthalpy changes for each individual step. This is possible because enthalpy is a state function, it depends only on the starting and ending states, not on the path taken to get from one to the other.

As an example, consider the combustion of carbon to form carbon dioxide. This can happen directly:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)} \quad \Delta H = -394 kJ/mol$$

The reaction can also occur indirectly, in two steps, where carbon monoxide is formed in the first step:

$$\mathrm{C(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO(g)} \quad \Delta H = -111 kJ/mol$$

Carbon monoxide reacts further with oxygen to form carbon dioxide in the second step:

$$\mathrm{CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)} \quad \Delta H = -283 kJ/mol$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{array}{ll} \text{step 1} & \mathrm{C(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO(g)} \\ \text{step 2} & \mathrm{CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)} \\ \text{sum} & \mathrm{C(s) + \cancel{CO(g)} + O_2(g) \longrightarrow \cancel{CO(g)} + CO_2(g)} \end{array}$$

Because the $\mathrm{CO(g)}$ produced in Step 1 is consumed in Step 2, the net change is:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.

$$\begin{array}{lll} \text{step 1} & \mathrm{C(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow \cancel{CO(g)}} & \Delta H = -111\,\mathrm{kJ/mol} \\ \text{step 2} & \mathrm{\cancel{CO(g)} + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)} & \Delta H = -283\,\mathrm{kJ/mol} \\ \text{sum} & \mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)} & \Delta H = -394\,\mathrm{kJ/mol} \end{array}$$

The principle of Hess's Law and enthalpy as a state function is shown graphically in Figure 5.6.1, the total enthalpy change is the same whether the reaction occurs in one step or two. This is the essence of Hess's Law: enthalpy changes are additive. It is important to specify the physical states of reactants and products in thermochemical equations, as enthalpy values depend on them.

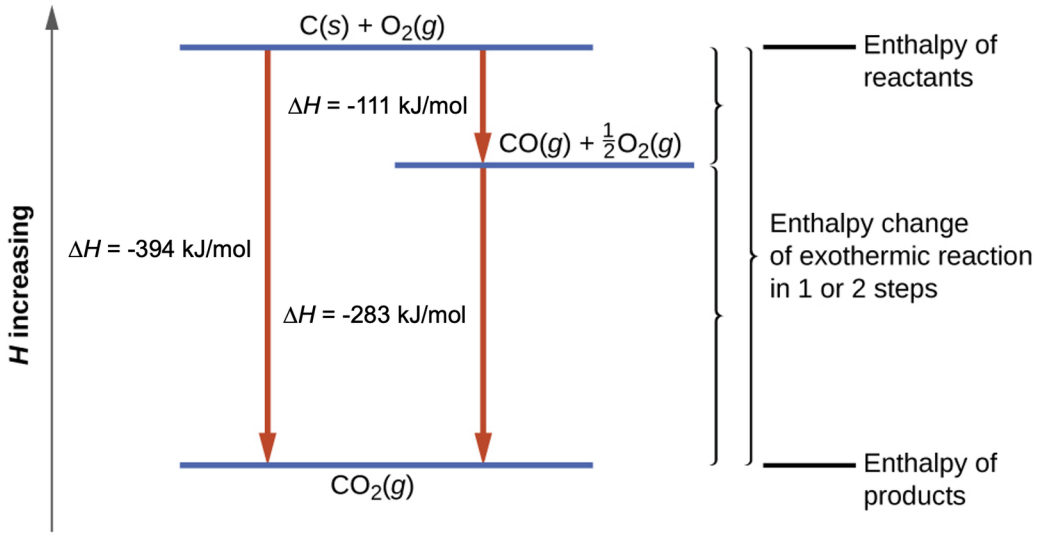


Figure 5.6.1: The formation of $\mathrm{CO_2\,(g)}$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Recall two important features of ΔH:

1. ΔH is directly proportional to the stoichiometric coefficients of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $\mathrm{NO_2\,(g)}$ is +33.2 kJ/mol:

   $$\tfrac{1}{2}\,\mathrm{N_2\,(g)} + \mathrm{O_2\,(g)} \longrightarrow \mathrm{NO_2\,(g)} \quad \Delta H = +33.2\,\mathrm{kJ/mol}$$

   If the reaction is doubled (stoichiometry is doubled), the enthalpy change doubles:

   $$\mathrm{N_2\,(g)} + 2\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{NO_2\,(g)} \quad \Delta H = +66.4\,\mathrm{kJ/mol}$$

   When a chemical equation is multiplied or divided by a number, the corresponding ΔH must be multiplied or divided by the same factor.

   - Note: The unit kJ/mol refers to the enthalpy change per mole of reaction as written, including all reactants and products in their specified stoichiometric coefficients. It does not refer to the enthalpy per mole of an individual substance.

2. Reversing a reaction changes the sign of the enthalpy change. The decomposition of $\mathrm{NO_2}(g)$ is the reverse of the formation reaction above:

   $$\mathrm{NO_2\,(g)} \longrightarrow \tfrac{1}{2}\,\mathrm{N_2\,(g)} + \mathrm{O_2\,(g)} \quad \Delta H = -33.2\,\mathrm{kJ/mol}$$

   Since the direction of heat flow is reversed, the enthalpy change has the same magnitude but the opposite sign.

Example 5.6.1

When carbon is burned with limited amounts of oxygen gas ($\mathrm{O_2}$), carbon monoxide (CO) is the main product:

$$(1)\;\; 2\,\mathrm{C\,(s)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO\,(g)} \quad \Delta H = -221.0\,\mathrm{kJ/mol}$$

When carbon is burned in excess $\mathrm{O_2}$, carbon dioxide ($\mathrm{CO_2}$) is produced:

$$(2)\;\; \mathrm{C\,(s)} + \mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} \quad \Delta H = -393.5\,\mathrm{kJ/mol}$$

What is ΔH for the following reaction?

$$2\,CO\,(g) + O_2\,(g) \longrightarrow 2\,CO_2\,(g)$$

Given: two balanced chemical equations and their ΔH values

Solution:

To apply Hess's Law, we need to combine the following equations to arrive at the desired reaction.

Step 1: Reverse the first reaction so that CO is a reactant and change the sign of ΔH:

$$(1)\;\; 2\,CO\,(g) \longrightarrow 2\,C\,(s) + O_2\,(g) \quad \Delta H = +221.0\ kJ/mol$$

Step 2: Multiply the second reaction by 2 so that the stoichiometric coefficient of CO_2 is 2, and adjust ΔH accordingly:

$$(2)\;\; 2\,C\,(s) + 2\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) \quad \Delta H = 2(-393.5\ kJ/mol) = -787.0\ kJ/mol$$

Step 3: Add the two reactions together:

step 1	$2\,CO\,(g) \longrightarrow \cancel{2C(s)} + \cancel{O_2(g)}$	$\Delta H = +221.0\ kJ/mol$
step 2	$\cancel{2C(s)} + \cancel{2}\,O_2\,(g) \longrightarrow 2\,CO_2\,(g)$	$\Delta H = -787.0\ kJ/mol$
sum	$2\,CO\,(g) + O_2\,(g) \longrightarrow 2\,CO_2\,(g)$	$\Delta H = -566.0\ kJ/mol$

Exercise 5.6.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \longrightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$

$$C_2H_2\,(g) + 2\,H_2\,(g) \longrightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the following reaction?

$$C_2H_4\,(g) + H_2\,(g) \rightarrow C_2H_6\,(g)$$

Answer available at the end of this section.

Exercise 5.6.2

Calculate ΔH for the process:

$$N_2\,(g) + 2\,O_2\,(g) \longrightarrow 2\,NO_2\,(g)$$

Using the following information:

$$N_2\,(g) + O_2\,(g) \longrightarrow 2\,NO\,(g) \quad \Delta H = 180.5\,kJ/mol$$

$$NO\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow NO_2\,(g) \quad \Delta H = -57.06\,kJ/mol$$

Answer available at the end of this section.

Example 5.6.2: Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$ClF\,(g) + F_2\,(g) \longrightarrow ClF_3\,(g) \quad \Delta H = ?$$

Use the following reactions to determine the ΔH for the above reaction:

$$2\,\mathrm{OF_2\,(g)} \longrightarrow \mathrm{O_2\,(g)} + 2\,\mathrm{F_2\,(g)} \quad \Delta H_{(ii)} = -49.4\,\mathrm{kJ/mol}$$
$$2\,\mathrm{ClF\,(g)} + \mathrm{O_2\,(g)} \longrightarrow \mathrm{Cl_2O\,(g)} + \mathrm{OF_2\,(g)} \quad \Delta H_{(iii)} = +214.0\,\mathrm{kJ/mol}$$
$$\mathrm{ClF_3\,(g)} + \mathrm{O_2\,(g)} \longrightarrow \tfrac{1}{2}\,\mathrm{Cl_2O\,(g)} + \tfrac{3}{2}\,\mathrm{OF_2\,(g)} \quad \Delta H_{(iv)} = +236.2\,\mathrm{kJ/mol}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i):

$$\mathrm{ClF\,(g)} + \mathrm{F_2\,(g)} \longrightarrow \mathrm{ClF_3\,(g)} \quad \Delta H = ?$$

Going from left to right in (i), we first see that $\mathrm{ClF}(g)$ is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$ which means that the ΔH change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \tfrac{1}{2}\,\mathrm{Cl_2O\,(g)} + \tfrac{1}{2}\,\mathrm{OF_2\,(g)} \quad \Delta H = \frac{1}{2}(214.0)\,\mathrm{kJ/mol} = +107.0\,\mathrm{kJ/mol}$$

Next, we see that $\mathrm{F_2}$ is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH changes sign and is halved:

$$\tfrac{1}{2}\,\mathrm{O_2\,(g)} + \mathrm{F_2\,(g)} \longrightarrow \mathrm{OF_2\,(g)} \quad \Delta H = +24.7\,\mathrm{kJ/mol}$$

To get $\mathrm{ClF_3}$ as a product, reverse (iv), changing the sign of ΔH:

$$\tfrac{1}{2}\,\mathrm{Cl_2O\,(g)} + \tfrac{3}{2}\,\mathrm{OF_2\,(g)} \longrightarrow \mathrm{ClF_3\,(g)} + \mathrm{O_2\,(g)} \quad \Delta H = -236.2\,\mathrm{kJ/mol}$$

Now check to make sure that these reactions add up to the reaction we want:

step 1	$\mathrm{ClF\,(g)} + \cancel{1/2O2(g)} \longrightarrow \cancel{1/2Cl2O(g)} + \cancel{1/2OF2(g)}$	$\Delta H = +107.0\,\mathrm{kJ/mol}$
step 2	$\cancel{1/2O2(g)} + \mathrm{F_2\,(g)} \longrightarrow \cancel{OF2(g)}$	$\Delta H = +24.7\,\mathrm{kJ/mol}$
step 3	$\cancel{1/2Cl2O(g)} + \cancel{3/2OF2(g)} \longrightarrow \mathrm{ClF_3\,(g)} + \cancel{O2(g)}$	$\Delta H = -236.2\,\mathrm{kJ/mol}$
sum	$\mathrm{ClF\,(g)} + \mathrm{F_2\,(g)} \longrightarrow \mathrm{ClF_3\,(g)}$	$\Delta H = -104.5\,\mathrm{kJ}$

Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH values will give the desired ΔH:

$$\Delta H = (+107.0) + (24.7) + (-236.2) = -104.5\,\mathrm{kJ/mol}$$

Exercise 5.6.3

Aluminum chloride can be formed from its elements:

$$2\,\mathrm{Al\,(s)} + 3\,\mathrm{Cl_2\,(g)} \longrightarrow 2\,\mathrm{AlCl_3\,(s)} \quad \Delta H = ?$$

Use the reactions here to determine the ΔH for reaction (i):

$$\mathrm{HCl\,(g)} \longrightarrow \mathrm{HCl\,(aq)} \quad \Delta H_{(ii)} = -74.8\,\mathrm{kJ/mol}$$
$$\mathrm{H_2\,(g)} + \mathrm{Cl_2\,(g)} \longrightarrow 2\,\mathrm{HCl\,(g)} \quad \Delta H_{(iii)} = -185\,\mathrm{kJ/mol}$$
$$\mathrm{AlCl_3\,(aq)} \longrightarrow \mathrm{AlCl_3\,(s)} \quad \Delta H_{(iv)} = +323\,\mathrm{kJ/mol}$$
$$2\,\mathrm{Al\,(s)} + 6\,\mathrm{HCl\,(aq)} \longrightarrow 2\,\mathrm{AlCl_3\,(aq)} + 3\,\mathrm{H_2\,(g)} \quad \Delta H_{(v)} = -1049\,\mathrm{kJ/mol}$$

Answer available at the end of this section.

Summary

Hess's Law states that the enthalpy change of an overall reaction is equal to the sum of the enthalpy changes of its individual steps (real or hypothetical). This principle follows from the fact that enthalpy is a state function—it depends only on the initial and final states, not the path taken.

Because enthalpy is an extensive property, changing the stoichiometry of a reaction will change the magnitude of ΔH. Reversing a chemical equation changes the sign of ΔH, but not its magnitude. The physical states of reactants and products must also be considered, since phase changes like melting or vaporization involve enthalpy changes of their own.

To apply Hess's Law, choose reactions with known enthalpy changes, adjust them to match the target reaction (by reversing or scaling as needed), and then add the corresponding ΔH values to find the overall enthalpy change.

Glossary

Hess's law
: Rule stating that if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps.

Answers

Exercise 5.6.1

Reverse the first reaction so that C_2H_4 appears as a reactant, matching the target equation. Change the sign of ΔH accordingly:

$$\begin{aligned} \mathrm{C_2H_4\,(g)} &\rightarrow \mathrm{C_2H_2\,(g) + H_2\,(g)} \quad \Delta H = +175.7\ \mathrm{kJ/mol} \\ \cancel{\mathrm{C2H2(g)}} + \cancel{2}\,\mathrm{H_2\,(g)} &\longrightarrow \mathrm{C_2H_6\,(g)} \qquad\qquad \Delta H = -312.0\ \mathrm{kJ/mol} \\ \mathrm{C_2H_4\,(g)} &\longrightarrow \cancel{\mathrm{C2H2(g)}} + \cancel{\mathrm{H2(g)}} \qquad \Delta H = +175.7\ \mathrm{kJ/mol} \\ \mathrm{C_2H_4\,(g) + H_2\,(g)} &\longrightarrow \mathrm{C_2H_6\,(g)} \qquad\qquad \Delta H = -136.3\ \mathrm{kJ/mol} \end{aligned}$$

Exercise 5.6.2

Multiplying the second equation by 2 will give the desired coefficient of NO_2:

$$\mathrm{2\,NO\,(g) + O_2\,(g) \longrightarrow 2\,NO_2\,(g)} \quad \Delta H = 2(-57.06\ \mathrm{kJ/mol}) = -114.12\ \mathrm{kJ/mol}$$

Adding this to the first equation yields the target reaction:

$$\mathrm{N_2\,(g) + O_2\,(g) \longrightarrow 2\,NO\,(g)} \quad \Delta H = 180.5\ \mathrm{kJ/mol}$$

$$\Delta H = -114.12\ \mathrm{kJ/mol} + 180.5\ \mathrm{kJ/mol} = +66.4\ \mathrm{kJ/mol}$$

Exercise 5.6.3

Multiply equation (iv) by 2 to get the desired product:

$$\mathrm{2\,AlCl_3\,(aq) \longrightarrow 2\,AlCl_3\,(s)} \quad \Delta H_{(iv)} = 2(+323) = +646\ \mathrm{kJ/mol}$$

To cancel $2\,AlCl_3$, use equation (v):

$$\mathrm{2\,Al\,(s) + 6\,HCl\,(aq) \longrightarrow 2\,AlCl_3\,(aq) + 3\,H_2\,(g)} \quad \Delta H_{(v)} = -1049\ \mathrm{kJ/mol}$$

Multiply equation (iii) by three to cancel $3\,H_2$ and have $3\,Cl_2$ as a reactant:

$$\mathrm{3\,H_2\,(g) + 3\,Cl_2\,(g) \longrightarrow 6\,HCl\,(g)} \quad \Delta H_{(iii)} = 3(-185) = -555\ \mathrm{kJ/mol}$$

Finally to cancel $HCl(g)$ and $HCl(aq)$, multiply equation (ii) by 6:

$$\mathrm{6\,HCl\,(g) \longrightarrow 6\,HCl\,(aq)} \quad \Delta H_{(ii)} = 6(-74.8) = -448.8\ \mathrm{kJ/mol}$$

The target equation is obtained by summing the four adjusted reactions, so the total enthalpy change is the sum of their ΔH values:

$$\Delta H_{(i)} = (+646\ \mathrm{kJ/mol}) + (-1049\ \mathrm{kJ/mol}) + (-555\ \mathrm{kJ/mol}) + (-448.8\ \mathrm{kJ/mol}) = -1407\ \mathrm{kJ/mol}$$

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5.7: Enthalpies of Formation

Learning Objectives

- Define standard state conditions for enthalpy measurements.
- Calculate enthalpy changes for reactions using Hess's Law and tabulated standard enthalpies of formation.

Measuring the enthalpy change for every possible chemical reaction would be impractical. Fortunately, Hess's Law allows us to calculate enthalpy changes using a smaller set of reference values: standard enthalpies of formation, ΔH_f^o.

Standard Enthalpies of Formation

A standard enthalpy of formation (ΔH_f^o, also called heat of formation) is the enthalpy change of the reaction describing the formation of a compound from its elements in their standard states:

$$elements \rightarrow compound\, \Delta H = \Delta H_f^o \tag{5.7.1}$$

The subscript "$_f$" in ΔH_f^o refers to a formation reaction and the superscript "^{o}" (called "naught") to the fact that the elements are all under standard state conditions, often defined as a total pressure of 1 atm for pure substances. The reactants in a formation reaction are the most stable form of the elements under standard conditions. For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), the most stable form at 1 atm is ($O_2\,(g)$). Similarly, the standard form of hydrogen is ($H_2\,(g)$) and for carbon, graphite, rather than diamond (Figure 5.7.1).



Figure 5.7.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure than diamond is. Hence graphite is the standard state of carbon.

As an example, here is the standard enthalpy of formation for carbon dioxide gas at 25°C:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = \Delta H_f^o = -393.5\ kJ/mol \tag{5.7.2}$$

By definition, the standard enthalpy of formation of any element in its standard state is zero because the reactants would be the same as the products:

$$O_2\,(g) \rightarrow O_2\,(g) \quad \Delta H_f^o = 0\ kJ/mol \tag{5.7.3}$$

Standard enthalpies of formation are often determined indirectly by measuring enthalpy changes for other reactions and applying Hess's Law. In many cases, compounds cannot be prepared directly from their elements in standard states. For example, the standard enthalpy of formation of glucose from its elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ/mol$$

This reaction does not proceed at a measurable rate, so the value of $\Delta H_f^o(glucose)$ = –1273.3 kJ/mol is obtained indirectly using Hess's Law and data from related reactions, such as the combustion of glucose.

Standard enthalpies of formation for a wide variety of compounds are listed in this reference table. These values are reported in kJ/mol of the compound formed.

Note on standard state conditions:

- While 1 atm is often used as standard state pressure, the official value adopted by the International Union of Pure and Applied Chemistry (IUPAC) is 1 bar (1 atm = 1.013 bar).
- Solutes in a solution have a standard state concentration of 1 mol/L, or 1 M.
- There is no standard state temperature; however, most standard thermodynamic quantities like the ones in the reference table are reported at 25°C. This is however not always the case, and it is important to check that all tabulated values used in a calculation are reported at the same temperature.

Example 5.7.1: Enthalpy of Formation

For each compound, write a balanced chemical equation corresponding to its formation reaction at standard conditions.

a. $\mathrm{HCl\,(g)}$
b. $\mathrm{MgCO_3\,(s)}$
c. $\mathrm{CH_3(CH_2)_{14}CO_2H\,(s)}$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that the stoichiometric coefficient of the product (compound of interest) is 1.

Solution:

a. Because the standard states of elemental hydrogen and elemental chlorine are $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$, respectively, the unbalanced chemical equation is

$$\mathrm{H_2\,(g) + Cl_2\,(g) \rightarrow HCl\,(g)}$$

Fractional coefficients are required in this case because ΔH^o_f values are reported per *1 mol* of the product, HCl. Multiplying both $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ by 1/2 balances the equation:

$$\mathrm{\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow HCl\,(g)}$$

b. The standard states of the elements in this compound are $\mathrm{Mg\,(s)}$, $\mathrm{C\,(s, graphite)}$, and $\mathrm{O_2\,(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg\,(s) + C\,(s, graphite) + O_2\,(g) \rightarrow MgCO_3\,(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg\,(s)} + \mathrm{C\,(s,\,graphite)} + \tfrac{3}{2}\,\mathrm{O_2\ (g)} \rightarrow \mathrm{MgCO_3\,(s)}$$

c. Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C\,(s,\,graphite)} + \mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \ \rightarrow \mathrm{CH_3(CH_2)_{14}CO_2H\,(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 molecule of palmitic acid, so the balanced chemical equation is

$$16\,\mathrm{C\,(s,\,graphite)} + 16\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \longrightarrow \mathrm{CH_3(CH_2)_{14}CO_2H\,(s)}$$

Exercise 5.7.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl\,(s)}$
b. $\mathrm{H_2SO_4\,(l)}$
c. $\mathrm{CH_3CO_2H\,(l)}$ (*acetic acid*)

Answer a available at the end of this section.

Calculating Enthalpy Changes Using ΔH_f^o

Standard enthalpies of formation can be used to calculate enthalpy changes for any reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction ΔH_{rxn}^o is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction:

$$aA + bB \rightarrow cC + dD \tag{5.7.4}$$

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The enthalpy change for the reaction can be calculated using the standard enthalpies of formation of the reactants and products:

$$\Delta H_{rxn}^o = \underbrace{\left[c\Delta H_f^o\,(C) + d\Delta H_f^o\,(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H_f^o\,(A) + b\Delta H_f^o\,(B)\right]}_{\text{reactants}} \tag{5.7.5}$$

More generally, we can express this as:

$$\Delta H_{rxn}^o = \sum m\Delta H_f^o\,(products) - \sum n\Delta H_f^o\,(reactants) \tag{5.7.6}$$

where the symbol $\sum$ means “sum of” and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively.

This equation is an application of Hess's Law which is built on the fact that enthalpy is a state function that only depends on the initial and final states—not on the specific steps taken to get from reactants to products. This equation also relies on all constituent elements in each ΔH_f^o chemical equation being in the same same state (i.e. standard state) such that if we were to write out the equations using Hess's law they would cancel leaving only the reactants and products. See Example 5.7.2 below for more details.

As an example, let’s calculate the enthalpy change for the combustion of glucose—the process that provides energy to our brains:

$$\mathrm{C_6H_{12}O_6\,(s)} + 6\,\mathrm{O_2\,(g)} \ \rightarrow 6\,\mathrm{CO_2\,(g)} + 6\,\mathrm{H_2O\,(l)}$$

Using Equation 5.7.6, we apply Hess's Law:

$$\Delta H^o_{rxn} = \left\{6\Delta H^o_f\left[CO_2\left(g\right)\right] + 6\Delta H^o_f\left[H_2O\left(l\right)\right]\right\} - \left\{\Delta H^o_f\left[C_6H_{12}O_6\left(s\right)\right] + 6\Delta H^o_f\left[O_2\left(g\right)\right]\right\}$$

From the reference table, the standard enthalpies of formation are:

- $\Delta H_f^\circ[CO_2(g)]$ = -393.5 kJ/mol
- $\Delta H_f^\circ[H_2O(l)]$ = -285.8 kJ/mol
- $\Delta H_f^\circ[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol
- $\Delta H_f^\circ[O_2(g)]$ = 0 kJ/mol (element in standard state)

Substituting into the equation:

$$\begin{aligned}\Delta H^o_{comb} &= \left[6\left(-393.5\ kJ/mol\right) + 6\left(-285.8\ kJ/mol\right)\right] - \left[-1273.3\ kJ/mol + 6\left(0\ kJ/mol\right)\right] \\ &= -2802.5\ kJ/mol\end{aligned}$$

So, the combustion of 1 mol of glucose releases 2802.5 kJ of energy.

Figure 5.7.2 shows a thermochemical cycle that helps us visualize this calculation.

- The upward arrow (on the left) represents converting reactants into their elements in standard states. This is the reverse of formation reactions and has an enthalpy change equal to the negative sum of ΔH_f° for the reactants.
- The downward arrows (on the right) represent forming the products from the elements in their standard states. This corresponds to the sum of ΔH_f° for the products.
- The green arrow across the diagram shows the direct enthalpy change for the overall combustion reaction: ΔH_{comb}°.

Because enthalpy is a state function, the total change in enthalpy is the same whether the reaction proceeds directly or through this two-step cycle:

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f\left(products\right) - \sum n\Delta H^o_f\left(reactants\right)$$

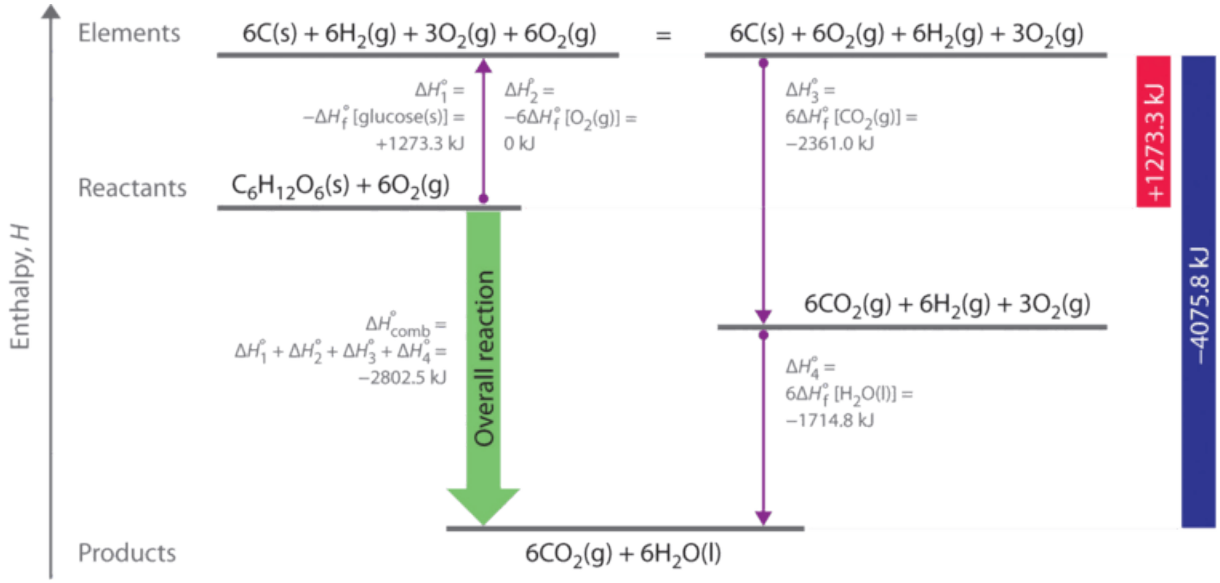


Figure 5.7.2: A Thermochemical Cycle for the Combustion of Glucose. This diagram shows two different pathways from reactants to products. The green arrow represents the direct combustion of glucose to carbon dioxide and water, with an enthalpy change of ΔH_{comb}°. The alternative path involves (1) converting the reactants into their elements in standard states (upward arrow, labeled ΔH^o_1 and ΔH^o_2), followed by (2) forming the products from those elements (downward arrows, labeled ΔH^o_3 and ΔH^o_4). According to Hess's Law, the overall enthalpy change is the same for both paths because enthalpy is a state function.

Example 5.7.2: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,\mathrm{NO_2\,(g)} + \mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{HNO_3\,(aq)} + \mathrm{NO\,(g)} \quad \Delta H^\circ = ?$$

Use the data in the reference table.

Solution

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants }) \\
&= \left[2\,\Delta H^\circ_f(\mathrm{HNO_3\,(aq)}) + \Delta H^\circ_f(\mathrm{NO\,(g)})\right] - \left[3\Delta H^\circ_f(\mathrm{NO_2\,(g)}) + \Delta H^\circ_f(\mathrm{H_2O\,(l)})\right] \\
&= [2(-207.4\,\mathrm{kJ/mol}) + 91.3\,\mathrm{kJ/mol}] - [3(33.2\,\mathrm{kJ/mol}) + (-285.8\,\mathrm{kJ/mol})] \\
&= -137.3\,\mathrm{kJ/mol}
\end{aligned}$$

Supporting Why the General Equation is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\,\mathrm{NO_2\,(g)}$ and $\mathrm{H_2O\,(l)}$ into their constituent elements (reverse of the formation reaction), and the formation of $2\,\mathrm{HNO_3\,(aq)}$ and $\mathrm{NO\,(g)}$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH°_f values:

$$\begin{aligned}
3\,\mathrm{NO_2\,(g)} &\longrightarrow \tfrac{3}{2}\,\mathrm{N_2\,(g)} + 3\,\mathrm{O_2\,(g)} && \Delta H^\circ_1 = -99.6\,\mathrm{kJ/mol}\left[-3\Delta H^\circ_f\,(\mathrm{NO_2})\right] \\
\mathrm{H_2O\,(l)} &\longrightarrow \mathrm{H_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} && \Delta H^\circ_2 = +285.8\,\mathrm{kJ/mol}\left[-\Delta H^\circ_f\,(\mathrm{H_2O})\right] \\
\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)} + 3\,\mathrm{O_2\,(g)} &\longrightarrow 2\,\mathrm{HNO_3\,(aq)} && \Delta H^\circ_3 = -414.8\,\mathrm{kJ/mol}\left[2\Delta H^\circ_f\,(\mathrm{HNO_3})\right] \\
\tfrac{1}{2}\,\mathrm{N_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} &\longrightarrow \mathrm{NO\,(g)} && \Delta H^\circ_4 = +91.3\,\mathrm{kJ/mol}\left[\Delta H^\circ_f(\mathrm{NO})\right]
\end{aligned}$$

Summing these four reactions gives the overall reaction we are interested in:

$$3\,\mathrm{NO_2\,(g)} + \mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{HNO_3\,(aq)} + \mathrm{NO\,(g)}$$

Summing the associated enthalpy changes:

$$\begin{aligned}
\Delta H^\circ_{rxn} &= \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 \\
&= (-99.6\,\mathrm{kJ/mol}) + (+285.8\,\mathrm{kJ/mol}) + (-414.8\,\mathrm{kJ/mol}) + (+91.3\,\mathrm{kJ/mol}) \\
&= -137.3\,\mathrm{kJ/mol}
\end{aligned}$$

The standard enthalpy change for this reaction is ΔH° = –137.3 kJ/mol.

This result was obtained by:

1. Multiplying the standard enthalpy of formation of each product by its stoichiometric coefficient and summing those values,
2. Multiplying the standard enthalpy of formation of each reactant by its stoichiometric coefficient and summing those values,
3. Subtracting the result from step 2 from the result in step 1.

This is exactly the procedure described in the general equation:

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants)$$

Example 5.7.3: Heat of Combustion

Palmitic acid, a long-chain fatty acid, is one of the major dietary sources of energy, alongside carbohydrates such as glucose. Its standard enthalpy of formation is ΔH_f°=−891.5 kJ/mol. Use the data in the reference table to calculate ΔH^0_{comb} for the combustion of palmitic acid ($CH_3(CH_2)_{14}CO_2H$):

$$C_{16}H_{32}O_2\,(s) + 23\,O_2\,(g) \rightarrow 16\,CO_2\,(g) + 16\,H_2O\,(l)$$

Which compound releases more energy per gram when combusted: glucose or palmitic acid?

Given: compound and ΔH_f^o values

Asked for: ΔH_{comb}^o per mole and per gram

Strategy:

A. Use Equation 5.7.6 and the values from the reference table to calculate ΔH_{comb}^o the energy released by the combustion of 1 mol of palmitic acid.
B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value for the combustion of glucose that was calculated above.

Solution:

A

$$C_{16}H_{32}O_2\,(s) + 23\,O_2\,(g) \rightarrow 16\,CO_2\,(g) + 16\,H_2O\,(l)$$

Using Equation 5.7.6 (products minus reactants) with ΔH^0_f values from Table T1:

$$\begin{aligned}\Delta H_{comb}^o &= \sum m\Delta H_f^o\,(products) - \sum n\Delta H_f^o\,(reactants)\\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\,)]\\ &- [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\,)]\\ &= -9977.3\ kJ/mol\end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H_{comb}^o\ \ per\ \ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ \ kJ/g$$

ΔH°_{comb} of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H_{comb}^o\ \ per\ \ gram = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ \ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This helps explain why fats are such efficient energy storage molecules in the body.

Exercise 5.7.2: Water–gas shift reaction

Use the reference table to calculate ΔH_{rxn}^o for the water–gas shift reaction, which is used industrially on an enormous scale to obtain H_2(g):

$$CO\ (\ g\ ) + H_2O\ (\ g\ ) \longrightarrow CO_2\,(g) + H_2\ (\ g\ )$$

Answer available at the end of this section.

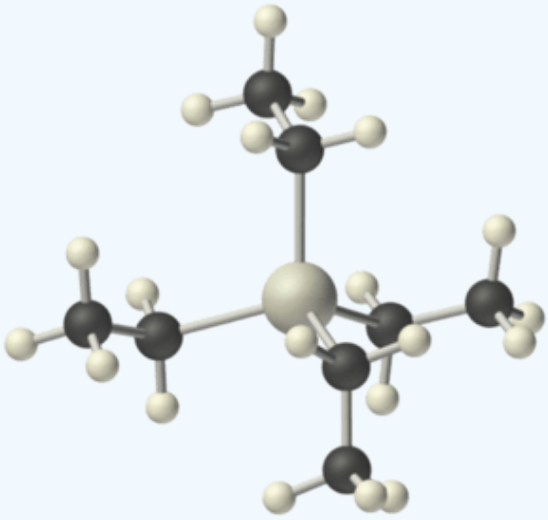
We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH_f^o which we cannot obtain otherwise. This procedure is illustrated in Example 5.7.4.

Example 5.7.4: Tetraethyllead

Tetraethyllead $(C_2H_5)_4Pb$ was once widely used as a gasoline additive to improve engine performance. Introduced in the 1920s, it was gradually phased out due to the serious health and environmental effects of lead pollution. Canada banned leaded gasoline for passenger vehicles in the early 1990s. The combustion reaction is as follows:

$$2\,(C_2H_5)_4Pb\,(l) + 27\,O_2\,(g) \longrightarrow 2\,PbO\,(s) + 16\,CO_2\,(g) + 20\,H_2O\,(l) \quad \Delta H = -19.29\ kJ/g$$

What is the standard enthalpy of formation of tetraethyllead, given this enthalpy of combustion and that ΔH_f^o of PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH_{comb}^o value

Asked for: ΔH_f^o of the reactant

Strategy:

A. Use Equation 5.7.6 to solve for ΔH^0_f of tetraethyl lead.
B. Convert ΔH_{comb}^o per gram given in the problem to ΔH_{comb}^o per mole by multiplying ΔH_{comb}^o per gram by the molar mass of tetraethyllead and adjusting to the stoichiometry of the reaction as written.
C. Use the reference table to obtain values of ΔH_f^o for the other reactants and products. Insert these values into the equation for ΔH_f^o of tetraethyl lead and solve the equation.

Solution:

A Equation 5.7.6 gives

$$\Delta H_{comb}^o = \left[2\Delta H_f^o\,(PbO) + 16\Delta H_f^o\,(CO_2) + 20\Delta H_f^o\,(H_2O)\right] - \left[2\Delta H_f^o\,((C_2H_5)_4\,Pb) + 27\Delta H_f^o\,(O_2)\right]$$

Solving for $\Delta H_f^o[(C_2H_5)_4Pb]$ gives

$$\Delta H_f^o\left(\left(C_2H_5\right)_4 Pb\right) = \Delta H_f^o\left(PbO\right) + 8\Delta H_f^o\left(CO_2\right) + 10\Delta H_f^o\left(H_2O\right) - \frac{27}{2}\Delta H_f^o\left(O_2\right) - \frac{\Delta H_{comb}^o}{2}$$

ΔH_f^o of PbO(s) is –219.0 kJ/mol. The values for the other substances can be found in the reference table.

B

The enthalpy of combustion is given as –19.29 kJ/g. This means that burning 1 gram of tetraethyllead releases 19.29 kJ of energy.

To determine the total energy change for the balanced reaction, which involves 2 equivalents of tetraethyllead, we need to:

1. Convert to kJ/mol using the molar mass (323.44 g/mol):

$$\begin{aligned}\Delta H_{rxn}^o &= \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right)\\ &= -6239\ kJ/mol\end{aligned}$$

2. Multiply by 2 (as per the balanced reaction):

$$\Delta H_{comb}^o = 2(-6239\ kJ/mol) = -12,478\ kJ/mol$$

This means that the combustion of 2 moles of tetraethyllead (or 1 mole of the balanced reaction as written) releases -12478 kJ of energy.

C Now insert the values into the rearranged Hess's Law equation to solve for the unknown $\Delta H_f^o[(\mathrm{C_2H_5})_4\mathrm{Pb}]$:

$$\begin{aligned}\Delta H_f^o\left[\left(C_2H_5\right)_4 Pb\right] &= [(-219.0\ kJ/mol) + 8(-393.5\ kJ/mol) + 10(-285.8\ kJ/mol)] + [-\frac{27}{2} \times 0] - \left[\frac{1}{2}(-12,478\ kJ/mol)\right]\\ &= -219.0\ kJ/mol - 3148\ kJ/mol - 2858kJ + 0kJ/mol + 6239\ kJ/mol = +14kJ/mol\end{aligned}$$

Exercise 5.7.3

Ammonium sulfate, $(\mathrm{NH_4})_2\mathrm{SO_4}$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,\mathrm{NH_3\,(g)} + \mathrm{H_2SO_4\,(aq)} \rightarrow (\mathrm{NH_4})_2\mathrm{SO_4\,(s)}$$

The value of ΔH_{rxn}^o is -179.4 kJ/mol. Use the data in the reference table to calculate the standard enthalpy of formation of ammonium sulfate.

Answer available at the end of this section.

Summary

The standard enthalpy of formation (ΔH_f^o) is the enthalpy change when 1 mole of a compound is formed from its elements in their most stable forms under standard conditions:

- 1 atm total pressure
- 1 M concentration for solutions

By definition, the standard enthalpy of formation of an element in its standard state is zero.

Standard enthalpies of formation are used to calculate standard enthalpies of reaction (ΔH_{rxn}^o) by subtracting the sum of enthalpies of formation of the reactants from that of the products:

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants)$$

This method relies on the fact that enthalpy is a state function, so the total enthalpy change depends only on the initial and final states, not on the path taken.

Glossary

standard enthalpies of formation ($\Delta H°_f$)
: The enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions.

standard state conditions
: The set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Answers

Exercise 5.7.1

$$\mathrm{Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g)\ \rightarrow NaCl\,(s)}$$
$$\mathrm{H_2\,(g) + \tfrac{1}{8}\,S_8\,(s) + 2\,O_2\ (\ g)\ \rightarrow H_2\ SO_4(\ l)}$$
$$\mathrm{2\,C\,(s) + O_2\,(g) + 2\,H_2\,(g) \longrightarrow CH_3CO_2H\,(l)}$$

Exercise 5.7.2**: Water–gas shift reaction**

$$\begin{aligned}\Delta H^o_{rxn} &= \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants)\\ &= [\Delta H^o_f(CO_2) + \Delta H^o_f(H_2)] - [\Delta H^o_f(CO) + \Delta H^o_f(H_2O)]\\ &= [-393.5\ kJ/mol + 0] - [-110.5\ kJ/mol + -241.8\ kJ/mol]\\ &= -41.2\ kJ/mol\end{aligned}$$

Exercise 5.7.3

$$\Delta H^o_{rxn} = \left[\Delta H^o_f\left((NH_4)_2SO_4\right)\right] - \left[2\Delta H^o_f\,(NH_3) + \Delta H^o_f\,(H_2SO_4)\right]$$

$$\Delta H^o_f\left((NH_4)_2SO_4\right) = \Delta H^o_{rxn} + \left[2\Delta H^o_f\,(NH_3) + \Delta H^o_f\,(H_2SO_4)\right] = -179.4\ kJ/mol\ +\ 2(-45.9\ kJ/mol)\ +\ (-909.3\ kJ/mol) = -1181\ kJ/mol$$

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5.8: Bond Energies

Learning Objectives

- Use average covalent bond energies to estimate enthalpies of reaction

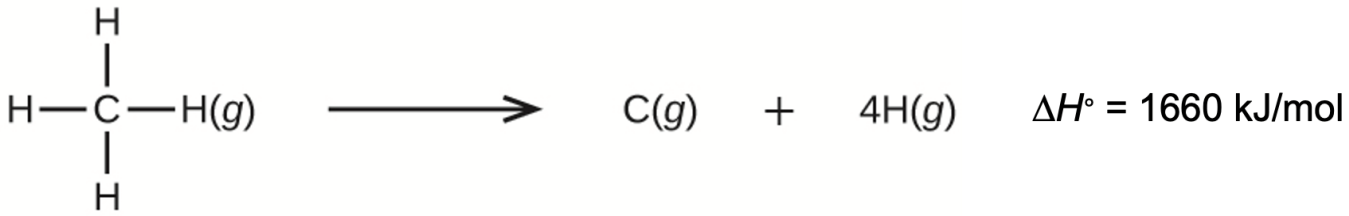
As we saw in Chapter 3, stable molecules exist because the atoms together have a lower energy than the same atoms apart. Covalent bonds hold atoms together within molecules. Breaking those bonds requires energy, and forming new ones releases energy. During a chemical reaction, some bonds in the reactants are broken (which requires energy), and new bonds in the products are formed (which releases energy). Whether the overall reaction is exothermic or endothermic depends on the relative amounts of energy used and released.

The strength of a covalent bond is measured by the energy required to break it. The bond energy or bond dissociation energy is the amount of energy required to break one mole of a specific bond in gaseous molecules under standard conditions. For example:

$$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(g)} \qquad D_{\mathrm{H-H}} = \Delta H^\circ = 436\,\mathrm{kJ/mol}$$

This means it takes 436 kJ to break one mole of $\mathrm{H-H}$ bonds in hydrogen gas. Note that this value applies to molecules in the gas phase, and it reflects the energy required to separate the bonded atoms completely. Because energy is required to break a bond, bond energies are always positive values.

Molecules with multiple atoms have many covalent bonds. For example, methane ($\mathrm{CH_4}$) contains four $\mathrm{C-H}$ bonds. Breaking all of them requires 1660 kJ per mole of methane:



Dividing by four, we estimate the average bond energy of a $\mathrm{C-H}$ bond as 1660/4 = 415 kJ/mol. This is an average because each bond doesn't necessarily require the same amount of energy to break. After the first bond is broken, the structure of the molecule changes, which can make the other bonds easier or harder to break. Bond energies used in tables are averages taken from many compounds, not precise values for a single molecule.

The strength of a bond depends on how strongly the two atoms attract the shared electrons. In general, the more electron pairs shared between two atoms, the stronger the bond. Triple bonds are stronger (and shorter) than double bonds. Double bonds are stronger (and shorter) than single bonds. This trend applies when the same two elements form different types of bonds.

Bond strength is also affected by which elements are bonded together. When comparing a series of bonds between carbon and different halogens, the bond strength decreases down the group. For example:

$\mathrm{C-F}$: 439 kJ/mol

$\mathrm{C-Cl}$: 330 kJ/mol

$\mathrm{C-Br}$: 275 kJ/mol

This is because larger atoms form longer bonds, which are generally weaker.

Average bond energies for common bonds are listed in Table $5.8.1$, and a comparison of bond lengths and bond strengths for some common bonds appears in Table $5.8.2$.

Table 5.8.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N=N	418	Si–Cl	359
H–P	320	N≡N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C=C	611	O–O	140	P–I	215
C≡C	837	O=O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C=N	615	O–Si	370	S–Br	215
C≡N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C=O	741	O–I	200	Cl–I	210
C≡O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 5.8.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å=0.1 nm)	Bond Energy (kJ/mol)
C–C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C–O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

We can use bond energies to estimate the enthalpy change of a reaction by comparing the energy needed to break bonds in the reactants to the energy released as new bonds form in the products.

$$\Delta H \approx \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$

- Breaking bonds requires energy (positive values)
- Forming bonds releases energy (subtract from the total)

Consider the following reaction:

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

Bonds broken:

- 1 $\mathrm{H{-}H}$ bond: 436 kJ/mol
- 1 $\mathrm{Cl{-}Cl}$ bond: 243 kJ/mol

Bonds formed:

- 2 $\mathrm{H{-}Cl}$ bonds: 2(432 kJ/mol) = 864 kJ/mol

$$\begin{aligned}\Delta H &\approx \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ &\approx [D_{\mathrm{H-H}} + D_{\mathrm{Cl-Cl}}] - 2D_{\mathrm{H-Cl}} \\ &\approx [436\,\mathrm{kJ/mol} + 243\,\mathrm{kJ/mol}] - 2(432\,\mathrm{kJ/mol}) \\ &= -185\,\mathrm{kJ/mol}\end{aligned}$$

The reaction is exothermic because the bonds formed in the products are stronger than the bonds broken in the reactants. This value is in good agreement with the ΔH calculated using the ΔH_f°(HCl) (ΔH_f°(HCl) = −92.3 kJ/mol, so ΔH° = 2(−92.3 kJ/mol) = −184.6 kJ/mol).

This approach gives a good estimate of the enthalpy change, especially for reactions where enthalpies of formation are unavailable. However, it does not account for all factors that affect the energy of a chemical reaction:

- Bond energies are averages, not exact values for a given molecule.
- It does not include intermolecular forces, such as hydrogen bonding or dipole interactions, which may be present before or after the reaction.
- It does not account for phase changes (e.g., condensation or vaporization) or differences in molecular structure and resonance.
- It assumes all substances are in the gas phase, because bond energies are measured for gas-phase molecules.

For more accurate results, we use standard enthalpies of formation or experimental data.

Example 5.8.1: Using Bond Energies to Calculate Approximate Enthalpy Changes

Methanol, $\mathrm{CH_3OH}$, is being explored as a cleaner alternative fuel. It can be produced from a mixture of carbon monoxide (CO) and hydrogen gas ($\mathrm{H_2}$), which is made by reacting steam with carbon at high temperatures.

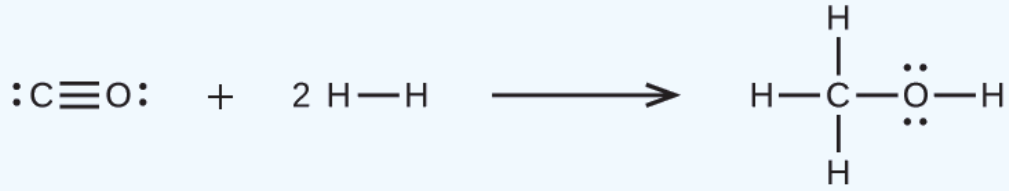
Using the bond energies in Table 5.8.2, estimate the enthalpy change, ΔH, for the following reaction:

$$\mathrm{CO\,(g) + 2\,H_2\,(g) \longrightarrow CH_3OH\,(g)}$$

Compare this value to the ΔH calculated using heats of formation from the reference table.

Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that ΔH for this reaction involves the energy required to break a $\mathrm{C{-}O}$ triple bond and two $\mathrm{H{-}H}$ single bonds, as well as the energy produced by the formation of three $\mathrm{C{-}H}$ single bonds, a $\mathrm{C{-}O}$ single bond, and an $\mathrm{O{-}H}$ single bond. We can express this as follows:

$$\begin{aligned}\Delta H &\approx \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \\ &\approx \left[D_{C\equiv O} + 2\left(D_{H-H}\right)\right] - \left[3\left(D_{C-H}\right) + D_{C-O} + D_{O-H}\right]\end{aligned}$$

Using the bond energy values in Table $5.8.2$, we obtain:

$$\begin{aligned}\Delta H &\approx [1080 + 2(436)] - [3(415) + 350 + 464] \\ &\approx -107 kJ/mol\end{aligned}$$

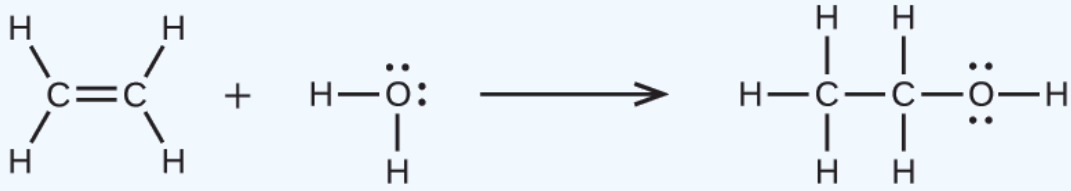
We can compare this value to the value calculated based on heats of formation from the reference table:

\[\begin{aligned}
\Delta H & =\left[\Delta H_{ f }^{\circ} \ce{(CH_3 OH (g))}\right]-\left[\Delta H_{ f }^{\circ}\ce{(CO (g))}+2 \times \Delta H_{ f }^{\circ}\ce{(H_2)}\right] \[4pt]
& =[-201.0\,\text{kJ/mol}]-[-110.5\,\text{kJ/mol}+2 \times 0] \[4pt]
& =-90.5 \,\text{kJ/mol}
\end{aligned} \nonumber \]

There is a noticeable difference between the two results. This is expected, because using bond energies gives only an approximate value. Bond energies are average values taken from many different compounds, and this method does not account for factors like intermolecular forces and phase changes. The value calculated using standard enthalpies of formation is more accurate and reflects real experimental data.

Exercise $5.8.1$

Ethyl alcohol (ethanol), $\mathrm{CH_3CH_2OH}$, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



Using the bond energies in Table $5.8.2$, calculate an approximate enthalpy change, ΔH, for this reaction.

Answer available at the end of this section.

Summary

Bond energy is the energy needed to break a specific bond in a gaseous molecule. Because bond energy values are often averaged across many compounds, they provide useful estimates but not exact values for individual molecules. Bond energies can be used to estimate the enthalpy change of a reaction by subtracting the energy released from forming product bonds from

the energy used to break reactant bonds. This method is useful when standard enthalpies of formation are not available, but it has limitations and works best for gas-phase reactions.

Glossary

bond energy
: The energy required to break a covalent bond in a gaseous substance; also called bond dissociation energy.

Answers

Exercise 5.8.1

Only the bonds that change during the reaction are included in the estimate; all other bonds are unchanged and cancel out.

$$\begin{aligned}\Delta H &\approx \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \\ &\approx [D_{C=C} + (D_{O-H})] - [D_{C-H} + D_{C-C} + D_{C-O}] \\ &\approx [611\,\text{kJ/mol} + 464\,\text{kJ/mol}] - [415\,\text{kJ/mol} + 345\,\text{kJ/mol} + 350\,\text{kJ/mol}] \\ &\approx -35\,\text{kJ/mol}\end{aligned}$$

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5.E: Thermochemistry (Exercises)

Energy and Its Conversion

Exercise $5.E.1$*

Why does hammering a piece of sheet metal cause the metal to heat up?

Answer available at the end of this section.

Exercise $5.E.2$**

What is the difference between heat and temperature?

Answer available at the end of this section.

Exercise $5.E.3$*

Is each of the following a form of kinetic or potential energy? Explain your reasoning.
a) The attraction between opposite charges in an ionic bond
b) A gas molecule moving through the air

Answer available at the end of this section.

The First Law of Thermodynamics

Exercise $5.E.4$*

Explain the sign convention for describing the internal energy of the system with respect to heat and work.

Answer available at the end of this section.

Exercise $5.E.5$*

What is the change in internal energy (ΔE) of a system that releases 325 J of heat and has 12 J of work done on it?

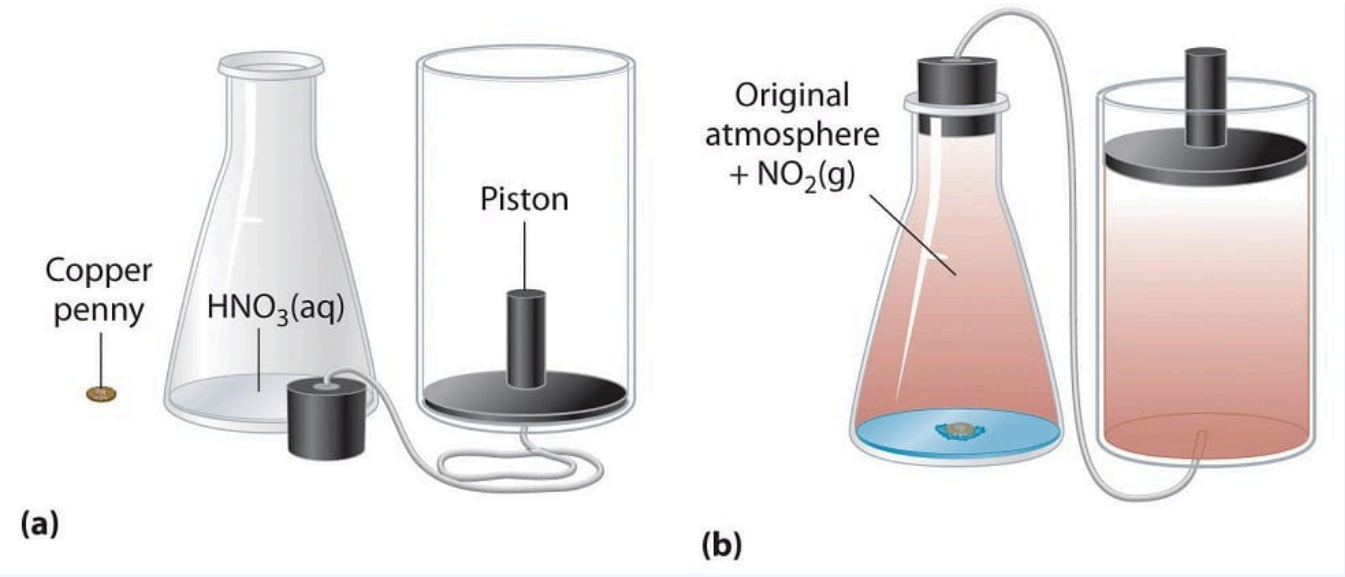
Answer available at the end of this section.

Exercise $5.E.6$**

Refer to the figure below, which shows a chemical reaction between a copper penny and concentrated nitric acid. The reaction produces NO_2 gas, which causes the piston to move upward, keeping the pressure constant.

a. Is the system doing work on the surroundings or is work being done on the system? Explain.

b. Would the value of w be positive or negative for this reaction? Explain.



(a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure.

Answer available at the end of this section.

Exercise $5.E.7$*

Argon gas expands from 3.25 L to 4.82 L against a constant external pressure of 2.30 atm. Calculate the work done by the gas, in joules.

Answer available at the end of this section.

Exercise $5.E.8$*

A sample of helium gas is compressed from 6.10 L to 2.75 L at a constant external pressure of 1.85 atm. Calculate the work done on the gas, in joules.

Answer available at the end of this section.

Enthalpy

Exercise $5.E.9$*

A scientist placed an unknown salt in a small amount of water in a beaker. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.

a. What is the sign of q for this reaction?

b. What is the sign of the enthalpy change (ΔH) for this reaction?

c. Is the dissolution exothermic or endothermic?

Answer available at the end of this section.

Exercise 5.E.10*

Heat is the flow of energy from one object to another due to a difference in temperature. Describe the direction of energy flow in:

a. an exothermic reaction

b. an endothermic reaction

Answer available at the end of this section.

Exercise 5.E.11*

State whether the process is endothermic or exothermic.

a. Water is added to sodium hydroxide pellets, and the flask becomes hot.
b. Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

Answer available at the end of this section.

Exercise 5.E.12*

Given the following thermochemical equation, what is ΔH for the reverse reaction?

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightarrow \mathrm{2\,NH_3\,(g)} \quad \Delta H = -91.8\,\mathrm{kJ/mol}$$

Answer available at the end of this section.

Exercise 5.E.13*

Given the following thermochemical equation,

$$\mathrm{C_6H_6\,(l)} \rightarrow \mathrm{3\,C_2H_2\,(g) + 6\,H_2O\,(l)} \quad \Delta H = 630.0\,\mathrm{kJ/mol}$$

a. Write the complete thermochemical equation for the reverse reaction.

b. What is ΔH for the following reaction?

$$\mathrm{6\,C_2H_2\,(g)} \rightarrow \mathrm{2\,C_6H_6\,(l)}$$

Answer available at the end of this section.

Exercise 5.E.14**

Consider the formation of hydrogen gas from the following reaction:

$$\mathrm{2\,H_2O\,(g)} \rightarrow \mathrm{2\,H_2\,(g) + O_2\,(g)} \quad \Delta H^\circ = +483.6\,\mathrm{kJ/mol}$$

How much heat is involved in the formation of 35.0 mL of $\mathrm{H_2}$ gas at 1.00 atm and 350 K? Is the heat absorbed or released?

Answer available at the end of this section.

Exercise 5.E.15*

Consider the following reaction:

$$2\,\mathrm{Al(s)} + 3\,\mathrm{Cl_2\,(g)} \rightarrow 2\,\mathrm{AlCl_3\,(s)} \quad \Delta H^\circ = -1408.4\,\mathrm{kJ/mol}$$

How many grams of $\mathrm{Al}(s)$ would have to react to release 325 kJ of energy?

Answer available at the end of this section.

Calorimetry

Exercise 5.E.16*

How much heat is required to heat a 28.4 g ice cube from –23.0 °C to –1.0 °C? The specific heat capacity of ice is 2.05 J/(g · K).

Answer available at the end of this section.

Exercise 5.E.17**

Using the data below, how much heat (q) is needed to raise the temperature of a 2.50 g piece of copper wire from 20.0 °C to 80.0 °C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount?

Specific heat capacities:

Cu: c = 0.386 J/(g · K)

Al: c = 0.900 J/(g · K)

Answer available at the end of this section.

Exercise 5.E.18**

Ethylene glycol, used as a coolant in automotive engines, has a specific heat capacity of 2.42 $J \cdot g^{-1} \cdot K^{-1}$. A 3.65 x 10^3 g sample of ethylene glycol releases 265 kJ of heat. If the initial temperature was 114.0 °C, what is the final temperature of the ethylene glycol?

Answer available at the end of this section.

Exercise 5.E.19**

A 360.0-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 is 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 (0.449 J/(g · °C)), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings). Water has a specific heat capacity of 4.18 J/(g · °C) and a density of 1.00 g/mL.

Answer available at the end of this section.

Exercise $5.E.20$**

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

The specific heat of copper is 0.385 J/(g · °C). Water has a specific heat capacity of 4.18 J/(g · °C) and a density of 1.00 g/mL.

Answer available at the end of this section.

Exercise $5.E.21$**

A 145-g piece of unknown metal is heated to 305.0 °C and then dropped into 275 mL of water at 21.0 °C. The final temperature of the metal and water is 38.0 °C.

Assuming no heat is lost to the surroundings, calculate the specific heat capacity of the metal.

Water has a specific heat capacity of 4.18 J/(g · °C) and a density of 1.00 g/mL.

Answer available at the end of this section.

Exercise $5.E.22$**

Dissolving 3.0 g of $\mathrm{CaCl_2}(s)$ in 150.0 g of water in a coffee cup calorimeter at 22.4 °C causes the temperature of the solution to rise to 25.8 °C.

What is Δ*H* (in kJ/mol) for the dissolution of $\mathrm{CaCl_2}$ in water? Is this an exothermic or endothermic process?

Assume that the calorimeter absorbs a negligible amount of heat and that the specific heat of the solution is the same as the specific heat of pure water (4.184 J/(g°C).

Answer available at the end of this section.

Exercise $5.E.23$***

When 100 mL of 0.200 M $\mathrm{NaCl}(aq)$ and 100 mL of 0.200 M $\mathrm{AgNO_3}(aq)$, both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms.

What is Δ*H* (in kJ/mol) for the precipitation reaction?

$$\mathrm{NaCl\,(aq) + AgNO_3\,(aq) \rightarrow NaNO_3\,(aq) + AgCl\,(s)}$$

Assume that the calorimeter absorbs a negligible amount of heat and that the specific heat of the solution is the same as the specific heat of pure water (4.184 J/(g · °C)). The density of the solution can be assumed to be 1.00 g/mL.

Answer available at the end of this section.

Exercise $5.E.24$**

When a 0.740-g sample of trinitrotoluene (TNT, molar mass: 213.13 g/mol), is combusted in a bomb calorimeter at constant volume, the temperature of the calorimeter rises from 23.4 °C to 26.9 °C. The total heat capacity of the calorimeter, including the water it contains, is 3358 J/°C.

What is the change in internal energy (ΔE) for the combustion of TNT, in kJ/mol?

Answer available at the end of this section.

Exercise $5.E.25$**

When 13.6 g of sucrose (molar mass: 342.3 g/mol) is burned in a bomb calorimeter, the temperature increases by 5.6°C. The heat capacity of the calorimeter is calculated at 3.40 kJ/°C. What is the change in internal energy (ΔE) for the combustion of sucrose, in kJ/mol?

Answer available at the end of this section.

Exercise $5.E.26$***

In a coffee cup calorimeter, 0.100 g of magnesium metal is added to 100.0 mL of 1.00 M HCl at 22.0 °C. The reaction that occurs is:

$$\mathrm{Mg\,(s) + 2\,HCl\,(aq)\ \rightarrow MgCl_2\,(aq) + H_2\,(g)}$$

The temperature of the solution rises to 27.5 °C.

Assume:

The specific heat capacity of the solution is 4.18 J/(g·°C)

The density of the solution is 1.00 g/mL

The calorimeter does not absorb a significant amount of heat

a. Identify the limiting reactant.
b. Calculate the amount of heat released by the reaction (in kJ).
c. Determine the enthalpy change (Δ*H*, in kJ/mol).

Answer available at the end of this section.

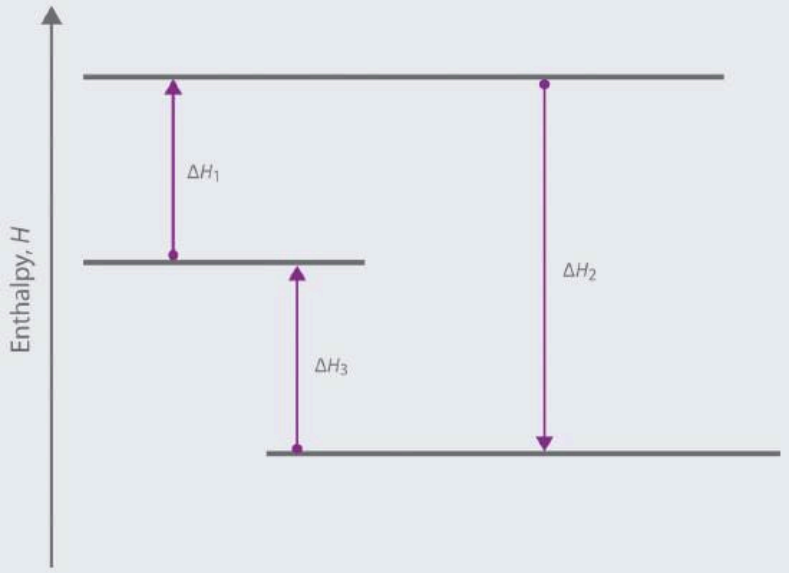
Hess's Law

Exercise $5.E.27$**

Based on the following energy diagram,

a. write an equation showing how the value of ΔH_2 could be determined if the values of ΔH_1 and ΔH_3 are known.

b. identify each step as being exothermic or endothermic.



Answer available at the end of this section.

Exercise 5.E.28**

The following sequence of reactions occurs to produce aqueous nitric acid:

$$4\,NH_3\,(g) + 5\,O_2\,(g) \rightarrow 4\,NO\,(g) + 6\,H_2O\,(l) \quad \Delta H = -907\,kJ/mol$$

$$2\,NO\,(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g) \quad \Delta H = -113\,kJ/mol$$

$$3\,NO_2\,(g) + H_2O\,(l) \rightarrow 2\,HNO_3\,(aq) + NO\,(g) \quad \Delta H = -139\,kJ/mol$$

The overall reaction is:

$$4\,NH_3\,(g) + 6\,O_2\,(g) + NO_2\,(g) \rightarrow 2\,HNO_3\,(aq) + 3\,NO\,(g) + 5\,H_2O\,(l) \quad \Delta H = ?$$

a. What is the ΔH for the reaction as written?

b. How much heat is released when 2.75 mol of HNO_3 is produced?

Answer available at the end of this section.

Exercise 5.E.29**

Calculate ΔH for the process:

$$Hg_2Cl_2\,(s) \rightarrow 2\,Hg\,(l) + Cl_2\,(g) \quad \Delta H = ?$$

Given:

$$Hg\,(l) + Cl_2\,(g) \rightarrow HgCl_2\,(s) \quad \Delta H = -224\,kJ/mol$$

$$Hg\,(l) + HgCl_2\,(s) \rightarrow Hg_2Cl_2\,(s) \quad \Delta H = -41.2\,kJ/mol$$

Answer available at the end of this section.

Exercise 5.E.30**

Calculate ΔH for the formation of acetylene (C_2H_2) from its elements:

$$2\,C\,(s) + H_2\,(g) \rightarrow C_2H_2\,(g) \quad \Delta H = ?$$

Given:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -393.5\,kJ/mol$$

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l) \quad \Delta H = -285.8\,kJ/mol$$

$$2\,C_2H_2\,(g) + 5\,O_2\,(g) \rightarrow 4\,CO_2\,(g) + 2\,H_2O\,(l) \quad \Delta H = -2599.6\,kJ/mol$$

Answer available at the end of this section.

Enthalpies of Formation

Exercise 5.E.31*

Write a balanced equation corresponding to the standard enthalpy of formation for each compound.

a. $C_2H_5OH(l)$

b. $CaCO_3(s)$

c. $N_2O_5(g)$

Answer available at the end of this section.

Exercise 5.E.32**

Using data from the reference table, determine ΔH°_{rxn} for each chemical reaction.

a.

$$2\,Na\,(s) + Pb(NO_3)_2\,(aq) \rightarrow 2\,NaNO_3\,(aq) + Pb\,(s)$$

b.

$$Na_2CO_3\,(s) + H_2SO_4\,(l) \rightarrow Na_2SO_4\,(s) + CO_2\,(g) + H_2O\,(l)$$

c.

$$2\,KClO_3\,(s) \rightarrow 2\,KCl\,(s) + 3\,O_2\,(g)$$

Answer available at the end of this section.

Exercise 5.E.33**

Consider the combustion reaction of toluene (C_7H_8) and the associated standard enthalpy change:

$$C_7H_8\,(l) + 9\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 4\,H_2O\,(l) \quad \Delta H^{\circ} = -3910\,kJ/mol$$

Given that the standard enthalpy of formation is -393.5 kJ/mol for CO_2(g) and -285.8 kJ/mol for H_2O(l), find the enthalpy of formation of C_7H_8(l).

Answer available at the end of this section.

Bond Energies

Exercise $5.E.34$*

Using the bond energies in Table 5.8.1, determine the approximate enthalpy change for each of the following reactions:

a. $\mathrm{H_2}(g) + \mathrm{Br_2}(g) \longrightarrow 2\,\mathrm{HBr}(g)$

b. $\mathrm{CH_4}(g) + \mathrm{I_2}(g) \longrightarrow \mathrm{CH_3I}(g) + \mathrm{HI}(g)$

Answer available at the end of this section.

Exercise $5.E.35$***

How does the bond energy of HCl differ from the standard enthalpy of formation of HCl(*g*)?

Answer available at the end of this section.

Additional Problems

Exercise $5.E.36$***

In a coffee cup calorimeter, 50.0 mL of 1.00 M HCl is mixed with 75.0 mL of 0.80 M NaOH, both at 22.6 °C. The temperature of the resulting solution rises to 27.7 °C. The calorimeter itself has a heat capacity of 41.8 J/°C.

$$\mathrm{NaOH\,(aq) + HCl\,(aq) \ \rightarrow NaCl\,(aq) + H_2O\,(l)}$$

Assume:

- Specific heat capacity of the solution is 4.18 J/(g·°C)
- Density of the solution is 1.00 g/mL
- All of the heat from the reaction is transferred to the calorimeter and solution.

a. Calculate the total amount of heat released by the reaction (in kJ), including the heat absorbed by the calorimeter.

b. Determine the enthalpy change (in kJ/mol).

c. Is this reaction exothermic or endothermic?

Answer available at the end of this section.

Exercise $5.E.37$***

A 1.50 g sample of ethanol (C_2H_5OH(l)) is combusted in a bomb calorimeter. The temperature of the calorimeter and its contents rises by 5.17 °C. The total heat capacity of the calorimeter is 9.21 kJ/°C.

The balanced combustion reaction is:

$$C_2H_5OH\,(l) + 3\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 3\,H_2O\,(l)$$

Given:

$\Delta H_f^\circ[CO_2(g)]$=−393.5 kJ/mol

$\Delta H_f^\circ[H_2O(l)]$=−285.8 kJ/mol

a. Calculate the amount of heat released when 1.50 g of ethanol is combusted.
b. Determine the ΔH° (in kJ/mol) for the combustion of ethanol. Assume $\Delta H^\circ \approx \Delta E^\circ$.
c. What is the standard enthalpy of formation of ethanol, $\Delta H_f^\circ[C_2H_5OH(l)]$ based on this data?

Answer available at the end of this section.

Exercise 5.E.38**

Consider the reaction: $2A(g) \rightarrow A_2(g)$

This reaction is carried out in a cylinder with a movable piston at constant external pressure.

a. Is heat absorbed or released during this reaction? What is the sign of q?
b. Does the system do work on the surroundings, or is work done on the system? What is the sign of w?
c. Based on your answers above, what is the sign of the change in internal energy (ΔE)?

Answer available at the end of this section.

Exercise 5.E.39***

The standard enthalpies of formation at 298 K are:

ΔH_f°[H(g)]=+218 kJ/mol

ΔH_f°[Cl(g)]=+121 kJ/mol

ΔH_f°[HCl(g)]=−92 kJ/mol

a. Write a balanced equation corresponding to the standard enthalpy of formation of H(g), Cl(g) and HCl(g).

b. Use Hess's Law and the equations from part (a) to construct a reaction pathway that represents the dissociation of HCl(g) into its atoms.

c. Use the given enthalpies of formation to estimate the bond energy of the H–Cl bond.

Answer available at the end of this section.

Exercise 5.E.40

a) Photovoltaics or solar panels can be used to generate energy from sunlight. Given sunlight's peak wavelength of 500 nm what is the energy of the photons being emitted at sun's peak wavelength?

b) Given that a standard residential solar panel array can produce 13 000 kJ of energy per hour, calculate how many moles of coal (approximated as carbon) are required to achieve the same amount of energy generation through combustion. Use the following reaction equation for your calculations.

$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ/mol}$

c) How many kilograms of CO_2 will be produced in the combustion to give 13 000 kJ of energy?

Answer a available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Green Chemistry Connection

The average Canadians' work commute is 8.7 kilometres one-way, with an average car output of 1.5 – 3.5 kg of CO_2 . The average electricity production from a solar panel array compared to a coal power plant saves the generation of ~1.5 kg of CO_2 every hour or a one-way trip to work!

Exercise $5.E.41$

Ethanol that is produced from biomass sources is added to gasoline in small quantities (5-10%) reduce the overall amount greenhouse gas emissions as the biomass used to make ethanol consumes carbon dioxide when it is grown. Let's compare the amount of carbon dioxide produced from the combustion of gasoline (approximated as isooctane) and ethanol.

Isooctane can be burned for energy according to the chemical equation below

$$25\ O_2(g) + 2\ C_8H_{18}(l) \rightarrow 16\ CO_2(g) + 18\ H_2O(l) \quad \Delta H = -10922 \text{ kJ}$$

a) Given the equation above calculate how many moles of carbon dioxide will be produced from 40.0 kg of isooctane (which is the gas tank size of a standard car)?

b) If the same gas tank is now filled with ethanol, calculate how many moles of carbon dioxide will be produced from the combustion of a tank of ethanol using the reaction equation below.

$$3\ O_2(g) + C_2H_6O(l) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)\ \Delta H_{comb} = -1367 \text{ kJ/mol}$$

c) Calculate how much energy can be produced upon combustion of one tank (40.0 kg) of isooctane?

d) Calculate how much energy is produced in the combustion of one tank (40.0 kg) of ethanol.

Answer a available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Answer d available at the end of this section.

Green Chemistry Connection

Note: A tank of ethanol produces less carbon dioxide than a tank of isooctane of the same mass, but it also produces less energy. As a result, the amount of carbon dioxide emitted per unit of energy released is nearly the same for the two fuels. The potential environmental benefit of ethanol is not that it produces substantially less carbon dioxide when burned, but that the carbon released during combustion was recently removed from the atmosphere by the biomass used to produce the ethanol. In contrast, burning gasoline releases carbon that has been stored underground in fossil

fuels for millions of years, increasing the amount of carbon dioxide in the atmosphere. Furthermore, ethanol's inherent oxygen content promotes a more complete combustion process, which helps to minimize localized toxic emissions such as carbon monoxide.

Answers

Exercise $5.E.1$*

When the hammer strikes the metal, its kinetic energy (energy of motion) is transferred to the metal. Some of this energy causes the atoms in the metal to vibrate more rapidly, which increases the thermal energy of the metal. As a result, the metal heats up.

Exercise $5.E.2$**

- Temperature is a measure of how hot or cold something is—it reflects the average kinetic energy of the particles in a substance.
- Heat is the transfer of energy from one object to another because of a difference in temperature.
- Heat flows from the hotter object to the cooler one until their temperatures are equal.

Exercise $5.E.3$*

a) Potential energy – The opposite charges are attracted to each other; this energy is stored in the arrangement.
b) Kinetic energy – The gas molecule is in motion.

Exercise $5.E.4$*

In thermodynamics, we use a system-surroundings perspective. The change in internal energy of the system (ΔE) depends on heat (q) and work (w): ΔE = q + w

- Heat added to the system → q is positive
- Heat lost by the system → q is negative
- Work done on the system (e.g., compression) → w is positive
- Work done by the system (e.g., expansion) → w is negative

This sign convention means that if the system gains energy, ΔE is positive. If it loses energy, ΔE is negative.

Exercise $5.E.5$*

The system releases heat, so q = -325 J.

Work is done on the system, so w = +12 J.

ΔE = q + w = -325 J + 12 J = -313 J.

The internal energy of the system decreases by 313 J.

Exercise $5.E.6$**

a. The system is doing work on the surroundings. As NO_2 gas forms, it pushes the piston upward, which requires energy. This means energy is being transferred from the system to the surroundings in the form of work.

b. The value of w is negative, because in thermodynamics, work done by the system (expansion against a constant pressure) is defined as negative. The system loses energy as it pushes the piston upward.

Exercise $5.E.7$*

$w = -P\Delta V = -2.30\ atm \cdot (4.82\ L - 3.25\ L) \cdot \left(\frac{101.32\ J}{L \cdot atm}\right) = -366\ J$

The negative sign means the gas did work on the surroundings by expanding.

Exercise $5.E.8$*

$w = -P\Delta V = -1.85\ atm \cdot (2.75\ L - 6.10\ L) \cdot \left(\frac{101.32\ J}{L \cdot atm}\right) = +628\ J$

The positive sign means work was done on the gas by the surroundings during compression.

Exercise $5.E.9$*

a. The temperature of the solution dropped, which means the surroundings (the water) lost heat. That heat was absorbed by the system (the dissolving salt), so q for the reaction is positive.

b. Because the process occurs at constant pressure, the heat flow q is equal to the change in enthalpy. So, the enthalpy change ΔH is also positive.

c. Since heat is absorbed by the system from the surroundings, the dissolution is endothermic.

Exercise $5.E.10$*

a. In an exothermic reaction, heat flows from the system to the surroundings.

b. In an endothermic reaction, heat flows from the surroundings to the system.

Exercise $5.E.11$*

a. Exothermic. The system releases heat to the surroundings, making the flask feel hot.

b. Endothermic. The system absorbs heat from the surroundings, causing the solution to feel cool.

Exercise $5.E.12$*

If the direction of a chemical equation is reversed, the sign of ΔH also reverses.

ΔH = 91.8 kJ/mol

Exercise $5.E.13$*

a.

$$3\,C_2H_2\,(l) \rightarrow C_6H_6\,(l) \quad \Delta H = -630.0\,kJ/mol$$

b. The given reaction is twice the reverse reaction, so we also double the enthalpy change:

ΔH = 2(-630.0 kJ/mol) = -1260.0 kJ/mol

Exercise $5.E.14$**

Step 1: Use the ideal gas law to find the moles of H_2:

$$n = \frac{PV}{RT} = \frac{(1.00\ atm)(0.0350\ L)}{(0.08206 \frac{L \cdot atm}{mol \cdot K})(350\ K)} = 0.00122 \text{ mol } H_2$$

Step 2: Scale enthalpy from reaction to quantity of H_2 produced:

Since 2 mol of H_2 corresponds to +483.6 kJ absorbed:

$$q = \frac{+483.6\,\text{kJ/mol}}{2\,\text{mol } H_2}\,(0.00122\,\text{mol}) = 0.295\,\text{kJ}$$

Since the value is positive, heat is absorbed by the system.

Exercise $5.E.15$*

Since 2 mol of Al corresponds to 1408.4 kJ released and the molar weight of Al is 26.98 g/mol:

$$\left(\frac{2\,\text{mol Al}}{-1408.4\,\text{kJ/mol}}\right)(-325\,\text{kJ})(26.98\,\text{g/mol}) = 12.5\,g$$

Exercise $5.E.16$*

$$q = mc\Delta T = (28.4\ g)\left(2.05\frac{J}{g \cdot K}\right)(-1.0\ ^\circ C - (-23.0\ ^\circ C)) = 1281\ \text{ J} = 1.28\ \text{ kJ}$$

Note: The temperature change (ΔT) is the same in Celsius and Kelvin.

$\Delta T = -1.0\ \ ^\circ C - (-23.0\ \ ^\circ C) = 22.0\ \ ^\circ C \quad \text{and} \quad \Delta T = 272\ \ K - 250\ \ K = 22\ \ K$

Exercise $5.E.17$**

For Cu: q = 57.9 J

For Al: q = 135 J

ΔT = T_f - T_i = 80.0 °C - 20.0 °C = 60.0 °C

The change in temperature in degrees Celsius is the same as the change in temperature in degrees K:

ΔT = T_f - T_i = (80.0 °C + 273)K - (20.0 °C + 273)K = 60.0 K

q = cmΔT

For Cu: q = 0.386 J/(g · K) (2.50 g)(60.0 K) = 57.9 J

For Al: q = 0.900 J/(g · K) (2.50 g)(60.0 K) = 135 J

Since the mass and temperature change are the same in both cases, the difference in heat required is due to the specific heat capacity of each metal. Aluminum has a higher specific heat capacity, so it requires more heat to raise its temperature by the same amount.

Exercise $5.E.18$**

$$q = mc\Delta T = -265\ kJ\left(\frac{1000\ J}{kJ}\right) = -265000\ J = (3.65\ \times 10^3\ g)\left(2.42\frac{J}{g \cdot K}\right)(T_f - 114.0°C)$$

$$T_f = 84.0°C$$

Note: The final temperature must be lower than the initial temperature because heat is lost from the system. This is consistent with the negative value of q.

Exercise $5.E.19$**

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 cooled, so it must have started at a higher temperature.

Assuming no heat is lost to the surroundings, all of the heat gained by the water came from the rebar:

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

Using the heat equation q = cmΔT, we can write:

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

The density of water is 1.00 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:

$$\left(0.449\frac{J}{g \cdot {}^\circ C}\right)(360.0\ g)\,(42.7\ ^\circ C - T_{i,\text{ rebar}}) = -\left(4.184\frac{J}{g \cdot {}^\circ C}\right)(425\ g)\,(42.7\ ^\circ C - 24.0\ ^\circ C)$$

$$T_{i,\text{ rebar}} = \frac{\left(4.184\frac{J}{g \cdot {}^\circ C}\right)(425\ g)\,(42.7\ ^\circ C - 24.0\ ^\circ C)}{\left(0.449\frac{J}{g \cdot {}^\circ C}\right)(360.0\ g)} + 42.7\ ^\circ C$$

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

Exercise $5.E.20$**

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

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

The density of water is 1.00 g/mL, so 390 mL of water = 390 g. Noting that the final temperature of both the copper and water is same, T_f, substituting known values yields:

$$\left(0.385\frac{J}{g \cdot {}^\circ C}\right)(248\ g)\,(T_f - 314\ ^\circ C) = -\left(4.18\frac{J}{g \cdot {}^\circ C}\right)(390\ g)\,(T_f - 22.6\ ^\circ C)$$

$$(95.48\frac{J}{{}^\circ C})T_f - 29981\ J = -1630\frac{J}{{}^\circ C}T_f + 36843\ J$$

$$T_f = 38.7\ ^\circ C$$

Exercise $5.E.21$**

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

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

The density of water is 1.00 g/mL, so 275 mL of water = 275 g.

$$c(145\ g)\,(38.0\ ^\circ C - 305.0\ ^\circ C) = -\left(4.18\frac{J}{g\cdot\ ^\circ C}\right)(275\ g)\,(38.0\ ^\circ C - 21.0\ ^\circ C)$$

$$c(-38715\ g\cdot ^\circ C) = -19541.5\ J$$

$$c = 0.505\frac{J}{g\cdot\ ^\circ C}$$

Exercise $5.E.22$**

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

Step 1: Determine amount of heat released to solution:

$$q_{\text{solution}} = cm\Delta T = 4.184\frac{J}{g\cdot\ ^\circ C}(150.0\ g + 3.0\ g)(25.8\ ^\circ C - 22.4\ ^\circ C) = 2177\ J = 2.18\ kJ$$

Step 2: Determine the moles of CaCl_2 that dissolve:

$$mol_{CaCl_2} = 3.0\ g\left(\frac{mol}{110.98\ g}\right) = 0.027\ mol$$

Step 3: Find ΔH by dividing by the moles of CaCl_2:

$$q_{\text{dissolving}} = -q_{\text{solution}} = -2.18\ kJ$$

$$\Delta H = \frac{-2.18\ kJ}{0.027\ mol} = -81\ kJ/mol$$

The process is exothermic, because heat is released when CaCl_2 dissolves, causing the temperature of the solution to increase.

Exercise $5.E.23$***

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

Step 1: Determine the amount of heat released to the solution. Note that the total volume is 100 mL + 100 mL = 200 mL and the density is 1.00 g/mL.

$$q_{\text{solution}} = cm\Delta T = 4.184\frac{J}{g\cdot\ ^\circ C}(200\ g)(23.5\ ^\circ C - 21.9\ ^\circ C) = 1339\ J = 1.34\ kJ$$

Step 2: Determine the moles of the limiting reactant:

In this case, NaCl and AgNO_3 react 1:1 and there are equal quantities of both.

$$mol_{NaCl} = 0.200\left(\frac{mol}{L}\right)(0.100\ L) = 0.0200\ mol$$

Step 3: Find ΔH by dividing by the moles that react:

$$q_{\text{rxn}} = -q_{\text{solution}} = -1.34\ kJ$$

$$\Delta H = \frac{-1.34\ kJ}{0.0200\ mol} = -67.0\ kJ/mol$$

Video solution

Exercise $5.E.24$**

$$q_{rxn} = -q_{calorimeter}$$

$$q_{calorimeter} = C\Delta T = 3358\frac{J}{^\circ C}(26.9\ ^\circ C - 23.4\ ^\circ C) = 11753\ J = 11.75\ kJ$$

$$mol_{TNT} = 0.74\ g\left(\frac{mol}{213.13\ g}\right) = 0.00347\ mol$$

$$\Delta E = \frac{-11.75\ kJ}{0.00347\ mol} = -3390\ kJ/mol$$

Exercise $5.E.25$**

$$q_{rxn} = -q_{calorimeter}$$

$$q_{calorimeter} = C\Delta T = 3.40\frac{kJ}{^\circ C}(5.6\ ^\circ C) = 19\ kJ$$

$$mol_{sucrose} = 13.6\ g\left(\frac{mol}{342.3\ g}\right) = 0.0397\ mol$$

$$\Delta E = \frac{-19\ kJ}{0.0397\ mol} = -480\ kJ/mol$$

Exercise $5.E.26$***

a. Find moles of each reactant:

$$0.100\,\text{g}\left(\frac{\text{mol}}{24.30\,\text{g}}\right) = 0.00412\,\text{mol Mg}$$

$$1.00\frac{\text{mol}}{\text{L}}\,(0.100\,\text{L}) = 0.100\,\text{mol HCl}$$

From the balanced equation, 2 mol HCl reacts with 1 mol Mg.

We need 0.00824 mol HCl to react with all the Mg, and we have 0.100 mol → excess HCl. Mg is the limiting reactant.

b. Total mass of solution = 100 g (from HCl solution) + 0.1 g Mg = 100.1 g.

$$q_{rxn} = -q_{\text{solution}} = -cm\Delta T = 4.18\frac{J}{g\cdot\ ^\circ C}(100.1\ g)(27.5\ ^\circ C - 22.0\ ^\circ C) = -2301\ J = -2.30\ kJ$$

c.

$$\Delta H = \frac{-2.30\ kJ}{0.00412\ mol} = -558\ kJ/mol$$

Exercise $5.E.27$**

a. $\Delta H_2 = (-\Delta H_1) + (-\Delta H_3)$

This follows from Hess's Law, which states that the total enthalpy change for a reaction is the sum of the enthalpy changes for the steps that lead to it. The two steps constituting reaction 2 here are the reverse of reaction 1 and the reverse of reaction 3.

b. ΔH_1 is endothermic, because the arrow points upward, indicating that enthalpy increases from reactants to products.

Therefore, $-\Delta H_1$ is exothermic (the reverse of an endothermic process).

ΔH_3 is also endothermic (arrow points upward), so $-\Delta H_3$ is exothermic as well.

So overall, ΔH_2 is the sum of two exothermic steps, and is exothermic.

Exercise $5.E.28$**

a. The sum of three steps give the overall reaction, so their ΔH values should also be added up:

ΔH = -907 kJ/mol + (-113 kJ/mol) + (-139 kJ/mol) = -1159 kJ/mol

b. 1159 kJ is released when 2 mol of HNO_3 is produced (based on the balanced equation), so:

$$q = \left(\frac{-1159\ kJ}{2\ mol}\right)(2.75\ mol) = -1594\ kJ$$

1594 kJ of heat is released.

Exercise $5.E.29$**

Reverse the first reaction:

$$\mathrm{HgCl_2\ (s) \rightarrow Hg\,(l) + Cl_2\,(g)} \quad \Delta H = -(-224\ \mathrm{kJ/mol})$$

Reverse the second reaction:

$$\mathrm{Hg_2Cl_2\,(s)\ \rightarrow Hg\,(l) + HgCl_2\,(s)} \quad \Delta H = -(-41.2\ \mathrm{kJ/mol})$$

Summing these modified reactions gives the desired reaction, so

ΔH = 224 kJ/mol + 41.2 kJ/mol = 265 kJ/mol

Exercise $5.E.30$**

1. Reverse and halve the third reaction to match the formation of 1 mol C_2H_2 as a product:

$$\mathrm{2\,CO_2\,(g) + H_2O\,(l)\ \rightarrow C_2H_2\,(g) + \tfrac{5}{2}\,O_2\,(g)} \quad \Delta H = -\frac{1}{2}(-2599.6) = +1299.8\ \mathrm{kJ/mol}$$

2. Multiply the first reaction by 2 to cancel out the 2 mol CO_2:

$$\mathrm{2\,C\,(s) + 2\,O_2\,(g)\ \rightarrow 2\,CO_2\,(g)} \quad \Delta H = 2(-393.5) = -787\ \mathrm{kJ/mol}$$

3. Adding these adjusted reactions and the second reaction as given:

$$\begin{aligned}
&\cancel{2CO2(g)} + \cancel{H2O(l)} \rightarrow \mathrm{C_2H_2\,(g)} + \cancel{5/2O2(g)} && \Delta H = -\frac{1}{2}(-2599.6) = +1299.8\ \mathrm{kJ/mol}\\
&\mathrm{2\,C\,(s)} + \cancel{2O2(g)} \rightarrow \cancel{2CO2(g)} && \Delta H = 2(-393.5) = -787\ \mathrm{kJ/mol}\\
&\mathrm{H_2\,(g)} + \cancel{1/2O2(g)} \rightarrow \cancel{H2O(l)} && \Delta H = -285.8\ \mathrm{kJ/mol}\\
&\mathrm{2\,C\,(s) + H_2\,(g) \rightarrow C_2H_2\,(g)} && \Delta H = +227\ \mathrm{kJ/mol}
\end{aligned}$$

Exercise $5.E.31$*

a.

$$\mathrm{2\,C\,(s) + 3\,H_2\,(g) + \tfrac{1}{2}\,O_2\,(g)\ \rightarrow C_2H_5OH\,(l)}$$

b.

$$\mathrm{Ca\,(s) + C\,(s) + \tfrac{3}{2}\,O_2\,(g)\ \rightarrow CaCO_3\,(s)}$$

c.

$$\mathrm{N_2\,(g) + \tfrac{5}{2}\,O_2\,(g)\ \rightarrow N_2O_5\,(g)}$$

Exercise $5.E.32$**

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants)$$

a.

$$\Delta H^o_{rxn} = [(2(-447.5\ \mathrm{kJ/mol}) + 0] - [0 + (-416.3\ \mathrm{kJ/mol})] = -478.7\ \mathrm{kJ/mol}$$

b.

$$\Delta H^o_{rxn} = [-1387.1\ \mathrm{kJ/mol} - 393.5\ \mathrm{kJ/mol} - 285.8\ \mathrm{kJ/mol}] - [-1130.7\ \mathrm{kJ/mol} - 909.3\ \mathrm{kJ/mol}] = -26.4\ \mathrm{kJ/mol}$$

c.

$$\Delta H^o_{rxn} = [(2(-436.5\ \mathrm{kJ/mol}) + 0] - [2(-397.7\ \mathrm{kJ/mol})] = -77.6\ \mathrm{kJ/mol}$$

Exercise $5.E.33$**

$$\begin{aligned}
\Delta H^o_{rxn} &= \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants) = -3910\ \mathrm{kJ/mol}\\
&= [7\Delta H_f(CO_2) + 4\Delta H_f(H_2O)] - [\Delta H_f(C_7H_8) + 9\Delta H_f(O_2)] = -3910\ \mathrm{kJ/mol}\\
&= [7(-393.5\ \mathrm{kJ/mol}) + 4(-285.8\ \mathrm{kJ/mol})] - [\Delta H_f(C_7H_8) + 0] = -3910\ \mathrm{kJ/mol}\\
&\Delta H_f(C_7H_8) = 12.3\ \mathrm{kJ/mol}
\end{aligned}$$

Exercise $5.E.34$*

a.

$$\begin{aligned}\Delta H &\approx \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ &\approx [D_{\text{H–H}} + D_{\text{Br–Br}}] - 2D_{\text{H–Br}} \\ &\approx [436\,\text{kJ/mol} + 190\,\text{kJ/mol}] - 2(370\,\text{kJ/mol}) \\ &\approx -114\,\text{kJ/mol}\end{aligned}$$

b.

$$\begin{aligned}\Delta H &\approx \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ &\approx [D_{\text{C–H}} + D_{\text{I–I}}] - [D_{\text{H–I}} + D_{\text{C–I}}] \\ &\approx [415\,\text{kJ/mol} + 150\,\text{kJ/mol}] - [295\,\text{kJ/mol} + 240\,\text{kJ/mol}] \\ &\approx 30\,\text{kJ/mol}\end{aligned}$$

Exercise $5.E.35$***

The bond energy of HCl is the energy required to break one mole of H–Cl bonds in the gas phase into individual atoms. This is always a positive value because breaking bonds requires energy:

$$\text{HCl}\,(\text{g}) \longrightarrow \text{H}\,(\text{g}) + \text{Cl}\,(\text{g})$$

The standard enthalpy of formation of HCl(g) is the enthalpy change when one mole of HCl(g) forms from hydrogen and chlorine in their standard states, diatomic gases:

$$\tfrac{1}{2}\,\text{H}_2\,(\text{g}) + \tfrac{1}{2}\,\text{Cl}_2\,(\text{g}) \longrightarrow \text{HCl}\,(\text{g})$$

This process involves breaking the H–H and Cl–Cl bonds and forming H–Cl bonds. The enthalpy of formation reflects the net energy change, and may be positive or negative depending on the relative strengths of the bonds broken and formed. For HCl(g), the process is exothermic, so ΔH_f° is negative.

In summary:

- Bond energy describes the energy required to break a specific bond (H–Cl) in isolation.
- Enthalpy of formation accounts for the overall energy change in forming a compound from elements in their standard states, involving bonds forming and breaking.

Exercise $5.E.36$***

Volume of solution = 50.0 mL + 75.0 mL = 125.0 mL. Since density is 1.00 g/mL, mass of solution is 125.0 g.

a.

$$-q_{rxn} = q_{\text{solution}} + q_{calorimeter} = cm\Delta T + C\Delta T = 4.18\frac{J}{g\cdot{}^\circ C}(125.0\ g)(27.7\ ^\circ C - 22.6\ ^\circ C) + 41.8\frac{J}{^\circ C}(27.7\ ^\circ C - 22.6\ ^\circ C) = 2878\ J$$
$$q_{rxn} = -2.88\ kJ$$

b. Moles of each reactant:

$$1.00\frac{mol}{L}(0.0500\ L) = 0.0500\ mol$$
$$0.80\frac{mol}{L}(0.0750\ L) = 0.0600\ mol$$

From the balanced equation (1:1 ratio), HCl is the limiting reactant.

$$\Delta H = \frac{-2.88\ kJ}{0.0500\ mol} = -57.6\ kJ/mol$$

c. The temperature of the solution increased, so heat was released to the surroundings. The reaction is exothermic.

Exercise $5.E.37$***

a.

$$q_{rxn} = -q_{calorimeter}$$
$$q_{calorimeter} = C\Delta T = 9.21\frac{kJ}{^\circ C}(5.17\ ^\circ C) = 47.6\ kJ$$
$$q_{rxn} = -47.6\ kJ$$

b.

$$\text{mol}_{\text{ethanol}} = 1.50\,\text{g}\left(\frac{\text{mol}}{46.07\,\text{g}}\right) = 0.0326\,\text{mol}$$
$$\Delta H^\circ = \frac{-47.6\ \text{kJ}}{0.0326\,\text{mol}} = -1460\ \text{kJ/mol}$$

c.

$$\begin{aligned}\Delta H^o_{rxn} &= \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants) = -1460\,\text{kJ/mol} \\ &= [2\Delta H_f(CO_2) + 3\Delta H_f(H_2O)] - [\Delta H_f(C_2H_5OH) + 3\Delta H_f(O_2)] = -1460\,\text{kJ/mol} \\ &= [2(-393.5\,\text{kJ/mol}) + 3(-285.8\,\text{kJ/mol})] - [\Delta H_f(C_2H_5OH) + 0] = -1460\,\text{kJ/mol} \\ &\Delta H_f(C_2H_5OH) = -184\,\text{kJ/mol}\end{aligned}$$

Exercise $5.E.38$**

a. The reaction forms a bond, which releases energy. Therefore, heat is released. q is negative.

b. The system contracts as gas particles combine (fewer moles of gas), so volume decreases, meaning the surroundings do work on the system. w is positive.

c. ΔE = q + w

Since q is negative and w is positive, the overall sign of ΔE depends on their relative sizes. Often, q is larger than w, but we can not be certain without values.

Exercise $5.E.39$***

a.

$$\frac{1}{2}\mathrm{H_2}(g) \longrightarrow \mathrm{H}(g)$$
$$\frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl}(g)$$
$$\frac{1}{2}\mathrm{H_2}(g) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{HCl}(g)$$

b. The desired reaction is:

$$HCl(g) \longrightarrow H(g) + Cl(g)$$

Using Hess's Law, we combine the formation of H(g) and Cl(g) with the reverse of the formation of HCl(g):

$$\begin{array}{ll} \frac{1}{2}\mathrm{H_2}(g) \longrightarrow \mathrm{H}(g) & \Delta H_f^\circ(H) = 218\,\mathrm{kJ/mol} \\ \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl}(g) & \Delta H_f^\circ(Cl) = 121\,\mathrm{kJ/mol} \\ \mathrm{HCl}(g) \longrightarrow \frac{1}{2}\mathrm{H_2}(g) + \frac{1}{2}\mathrm{Cl_2}(g) & -\Delta H_f^\circ(HCl) = +92\,\mathrm{kJ/mol} \\ \hline \mathrm{HCl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g) & \end{array}$$

c. The bond energy of H–Cl is equal to the enthalpy change for breaking the bond:

$$\begin{aligned} D_{\mathrm{HCl}} = -\Delta H^\circ &= \Delta H_f^\circ(H) + \Delta H_f^\circ(Cl) - \Delta H_f^\circ(HCl) \\ &= 218\,\mathrm{kJ/mol} + 121\,\mathrm{kJ/mol} - (-92\,\mathrm{kJ/mol}) \\ &= 431\,\mathrm{kJ/mol} \end{aligned}$$

Exercise $5.E.40$

$E = \frac{hc}{\lambda}$

$E = \frac{(6.626\times10^{-34}\ \mathrm{J\cdot s})(3.00\times10^{8}\ \mathrm{m/s})}{500\times10^{-9}\ \mathrm{m}}$

$E = 3.98 \times 10^{-19}\ \mathrm{J}$

Exercise $5.E.40$

$n = \frac{13000\ \mathrm{kJ}}{393.5\ \mathrm{kJ/mol}}$

$n = 33.0\ \mathrm{mol}$

Exercise $5.E.40$

$33.0\ \mathrm{mol\ C} \times \frac{1\ \mathrm{mol\ CO_2}}{1\ \mathrm{mol\ C}} \times \frac{44.01\ \mathrm{g}}{1\ \mathrm{mol}} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}$

$= 1.45\ \mathrm{kg\ CO_2}$

Exercise $5.E.41$

$$n(\mathrm{CO_2}) = \frac{40000\ \mathrm{g\ C_8H_{18}}}{(12.01\times8 + 1.00\times18)\ \mathrm{g/mol}} \times \frac{16\ \mathrm{mol\ CO_2}}{2\ \mathrm{mol\ C_8H_{18}}}$$

$n(\mathrm{CO_2}) = 2.81 \times 10^3\ \mathrm{mol}$

Exercise $5.E.41$

$$n(\mathrm{CO_2}) = \frac{40000\ \mathrm{g\ C_2H_6O}}{(12.01\times2 + 1.00\times6 + 16.00)\ \mathrm{g/mol}} \times \frac{2\ \mathrm{mol\ CO_2}}{1\ \mathrm{mol\ C_2H_6O}}$$

$n(\mathrm{CO_2}) = 1.74 \times 10^3\ \mathrm{mol}$

Exercise $5.E.41$

We can use the amount of $\mathrm{CO_2}$ produced by one tank of fuel and the stoichiometric relationship in the balanced equation to calculate the energy released.

$\frac{-10922\ \mathrm{kJ}}{16\ \mathrm{mol\ CO_2}}(2805\ \mathrm{mol}) = -1.91 \times 10^6\ \mathrm{kJ}$

Exercise $5.E.41$

We can use the amount of $\mathrm{CO_2}$ produced by one tank of fuel and the stoichiometric relationship in the balanced equation to calculate the energy released.

$\frac{-1367\ \mathrm{kJ}}{2\ \mathrm{mol\ CO_2}}(1738\ \mathrm{mol}) = -1.19 \times 10^6\ \mathrm{kJ}$

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6: CHEMICAL KINETICS

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6.1: Introduction

Reaction Rates to Medical Breakthroughs: The Kinetics Legacy of Maud Menten



phic with basic facts about Maud Menten, co-inventor of the Michaelis-Menten equation. Reproduced with permission from ıtion Archives, Accession 90-105, Science Service Records, Image No. SIA2008-5999.

Chemical reactions happen all around us, from metabolic pathways in living organisms to large-scale materials synthesis and drug discovery. Why do some reactions occur in seconds, while others take years? How can we control the rate at which they happen? These questions lie at the heart of chemical kinetics, the study of reaction rates.

One of the most influential scientists in this field was Maud Menten, a Canadian researcher and University of Toronto alumna. Menten earned her bachelor's, master's, and M.D. from U of T, making her one of the first Canadian women to qualify as a medical doctor. At a time when research opportunities for women in Canada were limited, she travelled to Germany to continue her scientific career. There, she collaborated with Leonor Michaelis to tackle a question that puzzled scientists: how do enzymes, the biological catalysts that power life, actually work?

Before Menten's work, little was known about how enzymes control reactions inside living organisms. Menten and Michaelis helped develop a model showing how enzymes bind to specific targets and speed up reactions. They were able to quantify how the rate of an enzyme-catalyzed reaction depends on substrate concentration, describing this mathematical relationship with the Michaelis-Menten equation.

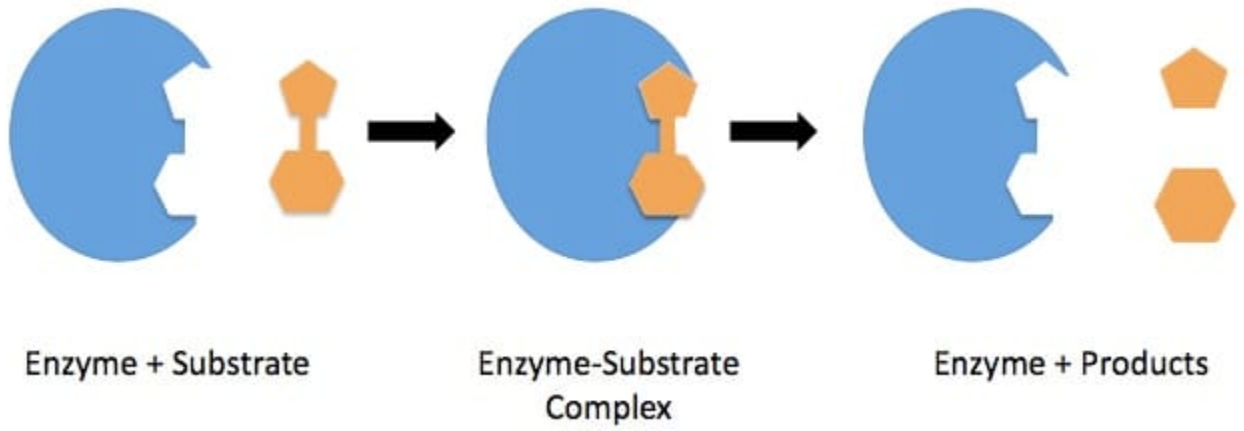


Figure 6.1.2**:** An illustration of the function of an enzyme. The enzyme binds its substrate, where a reaction occurs to transform it into product(s), which are subsequently released from the enzyme. Reproduced with permission from Wikimedia Commons under Creative Commons license CC-BY.

Today, more than a century later, Michaelis-Menten kinetics are still taught in science classrooms worldwide. Parameters from the Michaelis-Menten equation have become standard measures in the characterization of enzyme activity. Over time, this work has been applied beyond enzymes to other important biological interactions, such as antigen-antibody binding, DNA hybridization, and drug-target interactions. Maud Menten's breakthroughs not only advanced biological chemistry but also influenced medicine and industry. In this chapter, you'll learn the fundamentals of chemical kinetics: what reaction rates are, the factors that affect them, how they're measured, and how chemists use this knowledge to speed up reactions and control chemical processes.

Sources:

1. Le, H.; Algaze, S.; Tan, E. *Michaelis-Menten Kinetics*. Chemistry LibreTexts. https://chem.libretexts.org/Bookshelves/Biological_Chemistry/Supplemental_Modules_(Biological_Chemistry)/Enzymes/Enzymatic_Kinetics/Michaelis-Menten_Kinetics.
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3. *Leonor Michaelis and Maud Leonora Menten*. Science History Institute. https://www.sciencehistory.org/education/scientific-biographies/leonor-michaelis-and-maud-leonora-menten/.
4. *Maud L. Menten, MD PhD | CMHF*. https://www.cdnmedhall.ca/laureates/maudmenten.

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6.2: Reaction Rates

Learning Objectives

- Define chemical reaction rate
- Define and differentiate initial, instantaneous, and average rates as shown on a graph of concentration vs. time
- Relate the rates of change of any reactant and any product using the reaction stoichiometry

A rate measures how a quantity changes over time. Speed, for example, expresses the distance travelled per unit time, while wage represents the money earned per unit time. Similarly, the rate of a chemical reaction describes how quickly reactants are consumed or products are formed over time.

Reaction Rates

The rate of reaction is the change in the concentration of a reactant or product per unit time. Reaction rates are determined by measuring time-dependent changes in observable properties. For reactions involving gases, changes in volume or pressure can be measured. If a reaction involves a coloured substance, its rate can be monitored by changes in light absorption. For reactions with electrolytes, changes in solution conductivity can provide information about the rate.

The progress of a simple reaction (A → B) is shown in (Figure 6.2.1). The beakers show snapshots of the reaction mixture at 10-second intervals, while the graph plots the number of molecules of reactant (A) and product (B) over time. Each point on the graph corresponds to one beaker in (Figure 6.2.1). As the reaction proceeds, the concentration of A decreases and the concentration of B increases. The reaction rate is determined by the change in concentration of either species over a given time interval.

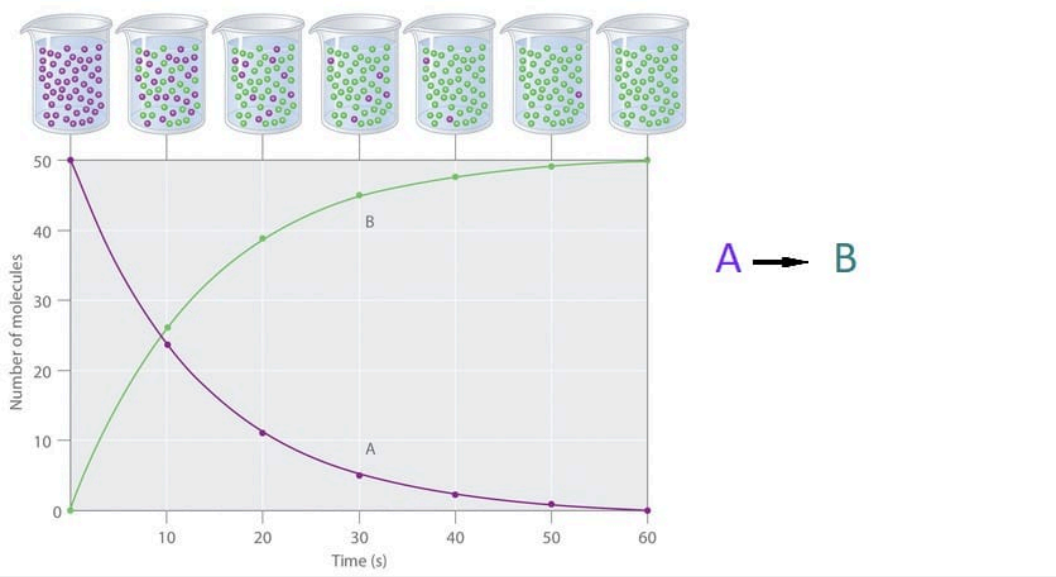


Figure 6.2.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed. The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 minute period.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

Square brackets indicate molar concentrations and the capital Greek delta (Δ) represents a change in value. By convention, reaction rates are always expressed as positive numbers. Since reactant concentrations decrease over time, the negative sign in -Δ[A]/Δt ensures the rate is reported as a positive quantity. This equation shows that the reaction rate is equal to the negative rate of disappearance of A and is also equal to the rate of appearance of B.

Consider the decomposition of hydrogen peroxide ($\mathrm{H_2O_2}$) in aqueous solution:

$$2\,\mathrm{H_2O_2}(aq) \longrightarrow 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g)$$

The rate of this reaction can be expressed in terms of the rate of change of [$\mathrm{H_2O_2}$]:

$$\begin{aligned}\text{rate of decomposition of } \mathrm{H_2O_2} &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[\mathrm{H_2O_2}_{t_2}] - [\mathrm{H_2O_2}_{t_1}]}{t_2 - t_1} \\ &= -\frac{\Delta[\mathrm{H_2O_2}]}{\Delta t}\end{aligned}$$

where:

- $[\mathrm{H_2O_2}_{t_1}]$ is the molar concentration of hydrogen peroxide at initial time t_1
- $[\mathrm{H_2O_2}_{t_2}]$ represents the molar concentration of hydrogen peroxide at a later time t_2
- $\Delta\,[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$)

Since the reactant concentration decreases as the reaction proceeds, Δ[$\mathrm{H_2O_2}$] is a negative quantity. The negative sign in the equation ensures the reaction rate is expressed as a positive quantity, consistent with standard convention. Figure 6.2.2 provides an example of data collected during the decomposition of $\mathrm{H_2O_2}$.

Time (h)	[H_2O_2] (mol L^{-1})	Δ[H_2O_2] (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
		−0.500	6.00	−0.0833
6.00	0.500			
		−0.250	6.00	−0.0417
12.00	0.250			
		−0.125	6.00	−0.0208
18.00	0.125			
		−0.062	6.00	−0.0103
24.00	0.0625			

Figure 6.2.2: The rate of decomposition of $\mathrm{H_2O_2}$ in an aqueous solution decreases as the concentration of $\mathrm{H_2O_2}$ decreases.

To obtain data for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over a 24-hour period at a constant temperature of 40 °C. Reaction rates were calculated for each time interval by dividing the change in concentration by the corresponding time increment, as shown for the first 6-hour period:

$$\frac{-\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{-(0.500\ \mathrm{mol/L} - 1.000\ \mathrm{mol/L})}{(6.00\ \mathrm{h} - 0.00\ \mathrm{h})} = 0.0833\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

As the reaction proceeds, the rate decreases over time. For the last 6-hour period, the reaction rate is:

$$\frac{-\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{-(0.0625\ \mathrm{mol/L} - 0.125\ \mathrm{mol/L})}{(24.00\ \mathrm{h} - 18.00\ \mathrm{h})} = 0.0104\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

These values show that the rate of reaction decreases with time.

Since reaction rates vary over time, it is important to specify which rate is being discussed:

- Average rate: the change in concentration of a reactant or product over a finite time interval.
- Instantaneous rate: the rate of reaction at a specific moment in time.
- Initial rate: the instantaneous rate at t=0, when the reaction first begins.

To illustrate this concept, consider a car slowing down as it approaches a stop sign. The initial rate of the car (analogous to the reaction's initial rate) is the speedometer reading when the brakes are first applied. A few seconds later, the instantaneous rate (analogous to the reaction rate at a given time) is the speedometer reading at that moment. The average rate over the entire deceleration period is the total distance travelled divided by the total time required to stop. Like a decelerating car, a chemical reaction's average rate falls between its initial and final rates.

The instantaneous rate of a reaction can be determined in two ways. If experimental conditions allow for the measurement of concentration changes over very short time intervals, then average rates, as previously described, can approximate instantaneous rates. Alternatively, as shown in the Figure 6.2.3, calculus can be used to determine the instantaneous rate of change at any given time by finding slope of a tangent line at that point.

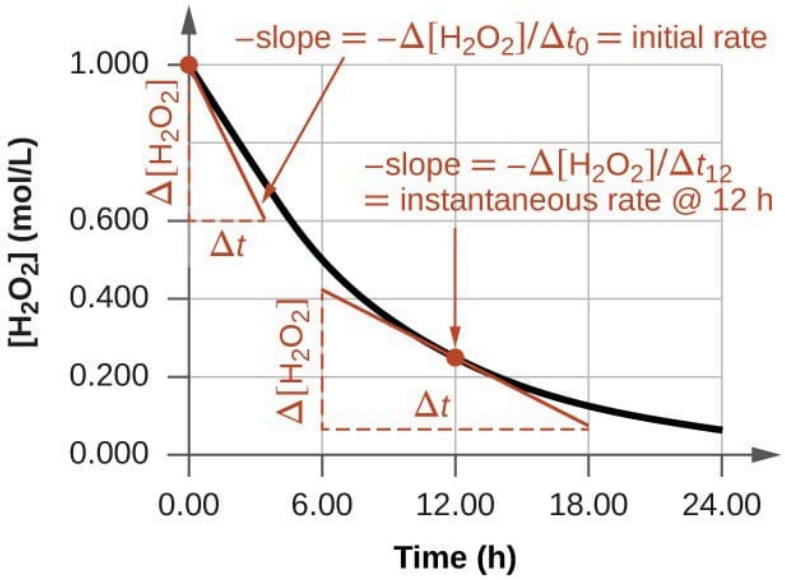


Figure 6.2.3: This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the negative of the slope of a line tangent to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at that particular time).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 6.2.4). These strips contain chemical reactants embedded in small pads, which undergo colour changes upon exposure to specific substances at sufficient concentrations. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step reaction:

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{catalyst}]{} C_6H_{10}O_6 + H_2O_2$$

$$2\,H_2O_2 + 2\,I^- \xrightarrow[\text{catalyst}]{} I_2 + 2\,H_2O + O_2$$

In the first reaction, glucose is oxidized to produce glucolactone and hydrogen peroxide. The hydrogen peroxide then oxidizes colourless iodide ions into brown iodine, which is visually detected. Some strips include additional reagents that enhance the colour contrast for easier interpretation.

These reactions are slow, but enzymes embedded in the test strip significantly speed up the process—a phenomenon known as catalysis, which will be discussed later in this chapter. A typical glucose test strip takes about 30 seconds for the colour to fully develop. Reading the strip too soon may lead to a false negative, underestimating the glucose concentration. Conversely, waiting too long may result in a false positive, as uncatalyzed oxidation by other substances in urine gradually darkens the test area.

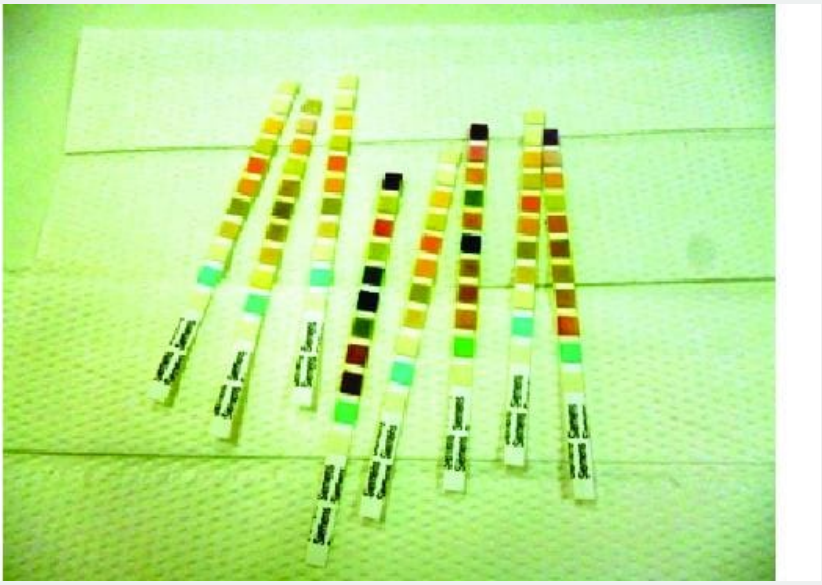


Figure 6.2.4: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman).

Relative Rates of Reaction

The rate of a reaction can be expressed in terms of the change in concentration of any reactant or product. The relative rates of reactant consumption and product formation are determined by the reaction's stoichiometry.

For a balanced reaction equation:

$$a\,\mathrm{A} + bB \longrightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

The reaction rate can be expressed using the stoichiometric coefficients:

$$\text{rate} = -\left(\frac{1}{\mathrm{a}}\right)\left(\frac{\Delta[\mathrm{A}]}{\Delta t}\right) = -\left(\frac{1}{\mathrm{b}}\right)\left(\frac{\Delta[\mathrm{B}]}{\Delta t}\right) = \left(\frac{1}{\mathrm{c}}\right)\left(\frac{\Delta[\mathrm{C}]}{\Delta t}\right) = \left(\frac{1}{\mathrm{d}}\right)\left(\frac{\Delta[\mathrm{D}]}{\Delta t}\right) \tag{6.2.1}$$

Since reaction rates are conventionally positive, the rate of disappearance of reactants is given a negative sign to reflect their decreasing concentration.

Consider the reaction:

$$2\,\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$$

The relative rates of reactant consumption and product formation follow from the stoichiometric coefficients. The relationship between the rates of nitrogen production and ammonia consumption is:

$$-\frac{1}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing).

Similarly, since three moles of $\mathrm{H_2}$ form for every one mole of $\mathrm{N_2}$ produced, the rate of $\mathrm{H_2}$ formation is three times the rate of $\mathrm{N_2}$ formation:

$$\frac{1}{3}\frac{\Delta[\mathrm{H_2}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Figure 6.2.5 illustrates the concentration changes over time for the decomposition of ammonia at 1100 °C. The slopes of the tangents drawn at *t* = 500 seconds confirm that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. For example, the rate of hydrogen production is observed to be approximately three times greater than the rate of nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/\mathrm{s}}{9.70 \times 10^{-7}\ M/\mathrm{s}} \approx 3$$

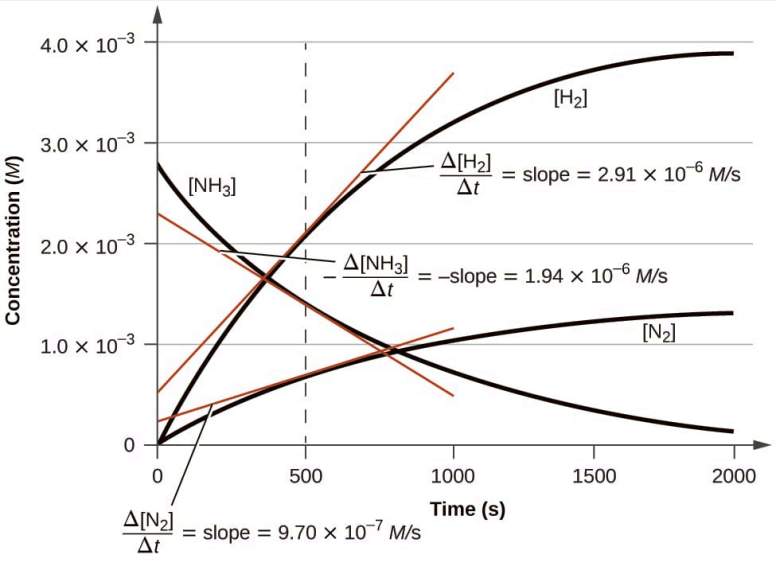


Figure 6.2.5: This graph shows the changes in concentrations of the reactants and products during the reaction $2\,\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{H_2}$. *The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s.*

Example 6.2.1

Consider the conversion of dinitrogen tetroxide, $\mathrm{N_2O_4}(g)$ to nitrogen dioxide, $\mathrm{NO_2}(g)$:

$$\mathrm{N_2O_4(\ g)\ \longrightarrow 2NO_2(\ g)}$$

Write the rate expression for the reaction in terms of disappearance of the reactants and appearance of the products.

Solution

For every one mole of reactant that disappears, two moles of product are formed. The rate of disappearance of $\mathrm{N_2O_4}$ must be must be half of the rate of appearance of $\mathrm{NO_2}$. The rate of reaction therefore may be expressed as:

$$\text{rate } = -\frac{\Delta[\,\mathrm{N_2O_4}]}{\Delta t} = \frac{1}{2}\frac{\Delta[\,\mathrm{NO_2}]}{\Delta t}$$

Example 6.2.2: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Exercise 6.2.1

The rate of formation of Br_2 is 6.0 × 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5\,Br^- + BrO_3^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer available at the end of this section.

Example 6.2.3: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 6.2.3 shows the rate of the decomposition of H_2O_2 over time:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at *t* = 11.1 h is determined to be 3.20 × 10^{-2} M/h, that is:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\,M\,h^{-1}$$

What are the instantaneous rates of production of H_2O and O_2 at 11.1 h?

Solution

From the stoichiometry of the reaction, we know:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

For O_2:

$$\frac{1}{2} \times 3.20 \times 10^{-2}\,M\,h^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2}\,M\,h^{-1}$$

For H_2O:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

$$\frac{\Delta[H_2O]}{\Delta t} = 3.2 \times 10^{-2}\,M\,h^{-1}$$

Exercise 6.2.2

If the rate of decomposition of ammonia, $\mathrm{NH_3}$, at 1150 K is 2.10×10^{-6} M/s, what are the rates of production of nitrogen and hydrogen?

$$2\,\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$$

Answer available at the end of this section.

Summary

The rate of a reaction can be expressed as the decrease in reactant concentration or the increase in product concentration per unit time. The relationships between different rate expressions are determined by the stoichiometric coefficients of the balanced equation.

The average rate is calculated as the change in concentration over a given time interval. The instantaneous rate refers to the rate at a specific moment in time and is determined by the slope of a tangent line on a concentration vs. time graph. The initial rate is the instantaneous rate at t=0, when the reaction begins.

Glossary

average rate of reaction
: The rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred.

initial rate of reaction
: The instantaneous rate of a chemical reaction at t=0 s (immediately after the reaction has begun).

instantaneous rate of reaction
: The rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time.

Answers

Exercise 6.2.1

$$-\frac{1}{5}\frac{\Delta[\mathrm{Br^-}]}{\Delta t} = -\frac{\Delta[\mathrm{BrO_3^-}]}{\Delta t} = -\frac{1}{6}\frac{\Delta[\mathrm{H^+}]}{\Delta t} = \frac{1}{3}\frac{\Delta[\mathrm{Br_2}]}{\Delta t} = \frac{1}{3}\frac{\Delta[\mathrm{H_2O}]}{\Delta t}$$

Exercise 6.2.2

1.05×10^{-6} M/s, $\mathrm{N_2}$ and 3.15×10^{-6} M/s, $\mathrm{H_2}$.

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6.3: Factors Affecting Reaction Rates

Learning Objectives

- Identify factors that affect reaction rates and explain how increasing surface area increases the speed of a reaction.

The rates at which reactants are consumed and products are formed can vary greatly depending on several factors. The most significant influences on reaction rate include:

- The surface area of solid reactants
- The temperature of the system
- The concentration of reactants
- The presence of a catalyst
- The chemical reactivity of the substances involved

Each of these factors affects how frequently and effectively reactant particles collide, which in turn influences reaction speed. While most of these will be explored in later sections, surface area is particularly relevant here.

Surface Area and Reaction Rate

For reactions involving solids, the rate depends on the surface area available for contact with other reactants. Reactions occur at the interface between phases, so a finely divided solid reacts more quickly than a single large piece of the same substance.

For example, iron powder reacts rapidly with acids, producing bubbles of hydrogen gas, whereas an iron nail reacts much more slowly (Figure $6.3.1$).



Figure $6.3.1$: In both test tubes, the following reaction takes place: $2\,\mathrm{Fe\,(s)} + 6\,\mathrm{HCl\,(aq)} \longrightarrow 2\,\mathrm{FeCl_3\,(aq)} + 3\,\mathrm{H_2\,(g)}$

(a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total area. (b) An iron nail reacts more slowly as indicated by fewer bubbles of gas forming.

In everyday life, we see that wood burns faster when finely chopped, and sawdust can even burn explosively due to its large surface area. Similarly, in cooking, chopping vegetables allows them to cook more quickly by increasing their surface area exposed to heat.

Other Factors Influencing Reaction Rate

- Temperature: Higher temperatures generally increase reaction rates, as seen when food spoils more quickly at room temperature than in a refrigerator.

- Concentration: In many reactions, increasing reactant concentration increases the rate by leading to more frequent collisions.
- Catalysts: Catalysts speed up reactions by providing an alternative pathway with lower activation energy, allowing the reaction to proceed more efficiently.
- Chemical Reactivity: Some substances react faster than others under the same conditions. For example, sodium reacts explosively with water, while calcium reacts more moderately, even though both metals undergo a similar reaction to form hydrogen gas and a hydroxide solution.

Except for chemical reactivity, the above factors will be explored in greater detail later in the chapter.

Summary

Several factors affect the rate of a chemical reaction. Surface area is particularly important for reactions involving solids—greater surface area leads to faster reactions by increasing contact between reactants. Factors like temperature, concentration, and catalysts also influence reaction rates and will be discussed in later sections.

Glossary

catalyst
: A substance that increases the rate of a reaction without itself being consumed by the reaction.

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6.4: Rate Laws

Learning Objectives

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

Form of the Rate Law and Reaction Orders

The rate of a reaction depends on the concentrations of reactants. A rate law is a mathematical expression that describes this relationship:

$$rate = k[A]^m[B]^n[C]^p \ldots$$

where [A], [B], and [C] represent the concentrations of the reactants, typically expressed in molarity. *k* is the rate constant, which does not depend on reactant concentrations but varies with temperature. The exponents *m*, *n*, and *p* are the reaction orders with respect to each reactant. Reaction orders are typically positive integers, and they define how the concentration of each reactant influences the reaction rate. All components of the rate law must be determined experimentally.

The exponents in the rate law determine the reaction order with respect to each reactant. Consider a reaction with the rate law:

$$\text{rate} = k[A]^m[B]^n$$

- If m is 1, the reaction is first order in *A*; if *m* is 2, the reaction is second order in *A*;
- If *n* is 1, the reaction is first order in *B*; if *n* is 2, the reaction is second order in *B*;
- If *m* or *n* is zero, the reaction is zero order in *A* or *B*, respectively (the rate is unaffected by the reactant concentration)

The overall reaction order is the sum of the individual orders. For example, if *m* = 1 and *n* = 1, the overall order of the reaction is second order (*m* + *n* = 2).

Consider the decomposition of hydrogen peroxide:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

Experimental data shows that the rate law for this reaction is:

$$\text{rate} = k[H_2O_2]$$

Since the exponent is 1, the reaction is first order in H_2O_2 and first order overall. The rate is directly proportional to $[H_2O_2]$; if the concentration doubles, the reaction rate also doubles.

Example 6.4.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

is second order in NO_2 and zero order in CO at 100 °C.

a) What is the rate law for the reaction?

b) How does doubling $[NO_2]$ affect the rate?

c) How does halving [CO] affect the rate?

Solution

a) The reaction will have the form:

$$\text{rate} = k[\mathrm{NO_2}^m][\mathrm{CO}]^n$$

The reaction is second order in $\mathrm{NO_2}$; thus *m* = 2. The reaction is zero order in CO; thus *n* = 0. The rate law is:

$$\text{rate} = k[\mathrm{NO_2}^2][\mathrm{CO}]^0 = k[\mathrm{NO_2}^2]$$

Remember that a number raised to the zero power is equal to 1, thus [CO]^0 = 1, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of $\mathrm{NO_2}$. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

b) Since the reaction is second order in $\mathrm{NO_2}$, doubling the concentration increases the rate by a factor of 4.

c) The reaction is zero order in CO, so halving the concentration will not affect the rate.

Exercise 6.4.1

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

has been experimentally determined to be:

$$\text{rate} = k[\mathrm{NO}]^2[\mathrm{H_2}]$$

What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer available at the end of this section.

Exercise 6.4.2

The reaction between methanol ($\mathrm{CH_3OH}$) and ethyl acetate ($\mathrm{CH_3CH_2OCOCH_3}$) follows the equation:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH}$$

Under certain conditions, the experimentally determined rate law is:

$$\text{rate} = k[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order?

Answer available at the end of this section.

These examples illustrate an important point: reaction orders cannot be determined from the coefficients in the balanced reaction. Reaction orders must be determined experimentally. How do we determine the orders in the rate law? In CHM 135, we will discuss two methods, starting with the method of initial rates.

Method of Initial Rates

The method of initial rates involves measuring the initial rate of a reaction under different reactant concentrations to see how the rate varies. These experiments typically involve changing the concentration of one reactant at a time to see how the rate of the

reaction varies with this change.

Consider the reaction and A and B:

$$A + B \rightarrow products$$

With the following experimental data collected over three runs:

Run	[A] (M)	[B] (M)	Rate (M/s)
1	0.0100	0.0100	0.0347
2	0.0200	0.0100	0.0694
3	0.0200	0.0200	0.2776

The rate law for this reaction will take the following form:

$$\text{rate} = k[A]^m[B]^n$$

Now we need to use the data to determine the values of *k*, *m*, and *n*. We will explore two different ways to approach this analysis.

Finding Reaction Orders By Inspection:

By comparing data sets where one reactant is held constant, we can determine the reaction order for each reactant:

- Finding the order with respect to A:

  Comparing Runs 1 and 2, [B] is unchanged (0.0100 M), so any change in rate is due to [A].
  Since [A] doubles and the rate also doubles, the reaction is first order in A (m = 1).

- Finding the order with respect to B:

  Comparing Runs 2 and 3, [A] is unchanged (0.0200M), so any change in rate is due to [B].
  Since [B] doubles and the rate increases by a factor of 4, the reaction is second order in B (n = 2).

This gives the rate law:

$$\text{rate} = k[A][B]^2$$

Mathematical Approach:

The reaction orders can also be determined mathematically by dividing two rate equations:

- Finding the order with respect to A, *m*, using the ratio of the rate laws for Runs 2 and 1:

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[A]_i^m[B]_i^n}{k[A]_j^m[B]_j^n}$$

$$\frac{0.0694\,\text{M/s}}{0.0347\,\text{M/s}} = \frac{\cancel{k}\,(0.0200\,\text{M})^m\,\cancel{(0.0100\,\text{M})^n}}{\cancel{k}\,(0.0100\,\text{M})^m\,\cancel{(0.0100\,\text{M})^n}}$$

$$2 = 2^m$$

In this case we can solve for *m* by inspection, *m* = 1, confirming the reaction is first order with respect to A.

- Finding the order with respect to B, *n*, using the ratio of the rate laws for Runs 3 and 2:

$$\frac{0.2776\,\mathrm{M/s}}{0.0694\,\mathrm{M/s}} = \frac{\cancel{k}\,(0.0200\,\mathrm{M})^m(0.0200\,\mathrm{M})^n}{\cancel{k}\,(0.0200\,\mathrm{M})^m(0.0100\,\mathrm{M})^n}$$

$$4 = 2^n$$

We might also be able to solve this equation by inspection, but in case the math is not so simple, or we want to double check, we can solve for the exponent by taking the logarithm of both sides (in this case we chose the $\log_{10}$):

$$\log(4) = \log(2^n)$$

Then we can use the rules for manipulating logarithms to solve for n:

$$\log(4) = n\log(2)$$

$$n = \frac{\log(4)}{\log(2)} = 2$$

We find *n* = 2, confirming the reaction is second order with respect to B.

$$\text{rate} = k[A][B]^2$$

The rate law indicates that the reaction is 1st order in A, 2nd order in B, and 3rd order overall.

Determining the rate constant

The rate constant k can be calculated by substituting any experimental data set into the rate law. Using Run 1:

$$0.0347\,M/s = k(0.0100\,M)(0.0100\,M)^2$$

Solving for k:

$$k = \frac{0.0347\,M/s}{(0.0100\,M)(0.0100\,M)^2} = 3.47 \times 10^5\,M^{-2}s^{-1}$$

Pay careful attention to the units of k as the units will change with the order of the reaction.

Example 6.4.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted by reactions with nitrogen oxides, contributing to the formation of the ozone hole over Antarctica (Figure 6.4.1). The rates of these reactions are critical in assessing their environmental impact.

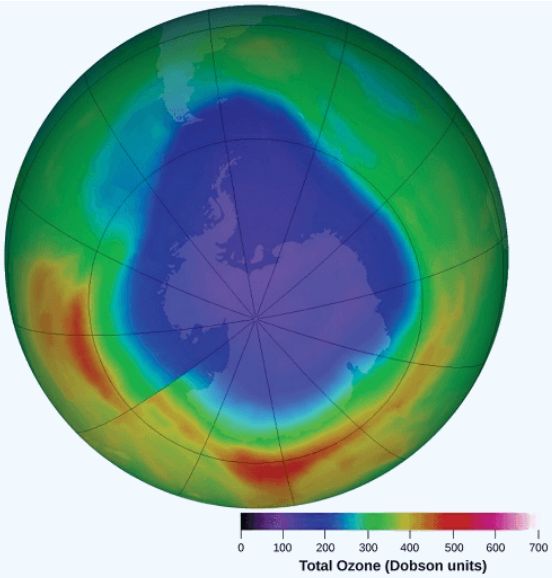


Figure 6.4.1: Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

One such reaction is the combination of nitric oxide (NO) with ozone ($\mathrm{O_3}$):

$$\mathrm{NO}(g)+\mathrm{O_3}(g) \longrightarrow \mathrm{NO_2}(g)+\mathrm{O_2}(g)$$

This reaction has been studied in the laboratory, and the following initial rate data were determined at 25 °C.

Trial	$[\mathrm{NO}]$ (M)	$[\mathrm{O_3}]$ (M)	$\frac{\Delta[\mathrm{NO_2}]}{\Delta t}$ $(\mathrm{M\,s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\mathrm{NO}]^m[\mathrm{O_3}^n]$$

We can determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. *Determine the value of* m *from the data in which* NO *varies and* O_3 *is constant.* In the last three experiments, $[\mathrm{NO}]$ varies while $[\mathrm{O_3}]$ remains constant. When $[\mathrm{NO}]$ doubles from trial 3 to 4, the rate doubles, and when $[\mathrm{NO}]$ triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to $[\mathrm{NO}]$, and *m* in the rate law is equal to 1.
2. *Determine the value of* n *from data in which* O_3 *varies and* NO *is constant.* In the first three experiments, $[\mathrm{NO}]$ is constant and $[\mathrm{O_3}]$ varies. The reaction rate changes in direct proportion to the change in $[\mathrm{O_3}]$. When $[\mathrm{O_3}]$ doubles from trial 1 to 2, the rate doubles; when $[\mathrm{O_3}]$ triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to $[\mathrm{O_3}]$, and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\mathrm{NO}]^1[\mathrm{O_3}^1] = k[\mathrm{NO}][\mathrm{O_3}]$$

3. *Determine the value of* k *from one set of concentrations and the corresponding rate.*

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \cancel{\text{M}}\ \text{s}^{-1}}{(1.00 \times 10^{-6}\ \cancel{\text{M}})(3.00 \times 10^{-6}\ \text{M})} \\ &= 2.20 \times 10^{7}\ \text{M}^{-1}\ \text{s}^{-1} \end{aligned}$$

The large value of *k* tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Exercise 6.4.3

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g)$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	$[\text{CH}_3\text{CHO}]$ (M)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}\ (\text{M s}^{-1})$
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer available at the end of this section.

Example 6.4.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\,\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\,\text{NOCl}(g)$$

Trial	[NO] (M)	$[\text{Cl}_2]$ (M)	$-\frac{\Delta[\text{NO}]}{2\Delta t}\ (\text{M s}^{-1})$
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2{}^n]$$

As in Example 6.4.2, we could approach this problem by inspection, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, we will use a more mathematical approach to determine the values of *m* and *n*:

Determine the value of m *from the data in which* NO *varies and* Cl_2 *is constant.* We can write the ratios with the subscripts i and j to indicate data from two different trials:

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[\text{NO}]_i^m[\text{Cl}_2{}_i^n]}{k[\text{NO}]_j^m[\text{Cl}_2{}_j^n]}$$

Using the third trial and the first trial, in which $[Cl_2]$ does not vary, gives:

$$\frac{\text{rate } 3}{\text{rate } 1} = \frac{0.00675\,M/s}{0.00300\,M/s} = \frac{k(0.15\,M)^m(0.10\,M)^n}{k(0.10\,M)^m(0.10\,M)^n}$$

After cancelling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675\,M/s}{0.00300\,M/s} = \frac{(0.15\,M)^m}{(0.10\,M)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

By taking the logarithm of both sides, we can determine the value of the exponent *m*:

$$\log(2.25) = \log(1.5^m)$$

By the rules of logs:

$$\log(2.25) = m\log(1.5)$$

$$m = \frac{\log(2.25)}{\log(1.5)} = 2$$

We can confirm the result, since $1.5^2 = 2.25$.

Determine the value of n *from data in which* Cl_2 *varies and* NO *is constant.*

$$\frac{\text{rate } 2}{\text{rate } 1} = \frac{0.00450\,M/s}{0.00300\,M/s} = \frac{k(0.10\,M)^m(0.15\,M)^n}{k(0.10\,M)^m(0.10\,M)^n}$$

Cancellation gives:

$$\frac{0.0045\,M/s}{0.0030\,M} = \frac{(0.15\,M)^n}{(0.10\,M)^n}$$

which simplifies to:

$$1.5 = (1.5)^n$$

Thus *n* must be 1, and the form of the rate law is:

$$\text{Rate} = k[\text{NO}]^m[\text{Cl}_2{}^n] = k[\text{NO}]^2[\text{Cl}_2]$$

Determine the numerical value of the rate constant k *with appropriate units.*

To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

$$0.00300\ \text{M/s} = k(0.10\ \text{M})^2(0.10\ \text{M})^1$$
$$k = 3.0\ \text{M}^{-2}\ \text{s}^{-1}$$

Exercise 6.4.4

Use the provided initial rate data to derive the rate law for the reaction:

$$\text{OCl}^-(aq) + \text{I}^-(aq) \longrightarrow \text{OI}^-(aq) + \text{Cl}^-(aq)$$

Trial	[OCl^-] (M)	[I^-] (M)	Initial Rate (M/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant *k* with appropriate units for this reaction.

Answer available at the end of this section.

Reaction Order and Rate Constant Units

In some cases, the reaction orders in the rate law match the stoichiometric coefficients of the balanced equation, but this is not generally true. Reaction orders must be determined experimentally and are not derived from the overall reaction equation.

Here are some examples of experimentally determined rate laws:

$$\mathrm{NO_2 + CO \longrightarrow NO + CO_2} \quad \text{rate} = k[\mathrm{NO_2}^2] \qquad \mathrm{CH_3CHO \longrightarrow CH_4 + CO} \quad \text{rate} = k[\mathrm{CH_3CHO}]^2$$
$$\mathrm{2\,N_2O_5 \longrightarrow 2\,NO_2 + O_2} \quad \text{rate} = k[\mathrm{N_2O_5}] \qquad \mathrm{2\,NO_2 + F_2 \longrightarrow 2\,NO_2F} \quad \text{rate} = k[\mathrm{NO_2}][\mathrm{F_2}]$$
$$\mathrm{2\,NO_2Cl \longrightarrow 2\,NO_2 + Cl_2} \quad \text{rate} = k[\mathrm{NO_2Cl}]$$

> It is important to note that *rate laws are determined by experiment only and are not reliably predicted by the reaction stoichiometry of the overall reaction.*

The reaction orders in the rate law will determine the units of the rate constant *k*. Reaction rate always has units of concentration over time, typically M/s or M s^{-1}. This means that the rate constant, *k*, needs to reconcile the concentration units in the rate law, as determined by the reaction orders, to ensure the overall rate has the correct units. For example, in a second-order reaction, the units of *k* are $M^{-1}s^{-1}$, while in a third-order reaction, the units are $M^{-2}s^{-1}$. Rather than memorizing these units, you can determine them by substituting units into the rate law and solving for *k*. The table below summarizes the units of *k* for common reaction orders:

Table 6.4.1*: Rate Constants for Common Reaction Orders*

Overall Reaction Order	Units of *k*
$(m+n)$	$\mathrm{M}^{1-(m+n)}\mathrm{s}^{-1}$
zero	M s^{-1}
first	s^{-1}
second	M^{-1} s^{-1}
third	M^{-2} s^{-1}

The units of *k* can also be written using mol/L instead of M, and different time units (e.g., minutes, hours, days) may be used depending on the experiment.

Summary

Rate laws describe how reaction rates depend on reactant concentrations and must be determined experimentally rather than predicted from the stoichiometry of the overall reaction. Reaction orders indicate how changes in reactant concentration will affect the rate of the reaction. The overall order of a reaction is the sum of all the individual reaction orders. While most reactions are zero, first, or second order, fractional and negative reaction orders are possible. The method of initial rates can be used to determine reaction orders by systematically varying reactant concentrations and observing their effect on the initial rate.

Glossary

method of initial rates
: The use of a more explicit algebraic method to determine the orders in a rate law.

overall reaction order
: The sum of the reaction orders for each substance represented in the rate law.

rate constant (*k*)
: Proportionality constant in the relationship between reaction rate and concentrations of reactants.

rate law
: A mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants; also called rate equation.

reaction order
: The value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on).

Answers

Exercise 6.4.1

- order in NO = 2;
- order in $\mathrm{H_2}$ = 1;
- overall order = 3

Exercise 6.4.2

- order in $\mathrm{CH_3OH}$ = 1;
- order in $\mathrm{CH_3CH_2OCOCH_3}$ = 0;
- overall order = 1

Exercise 6.4.3

$\mathrm{rate} = k[\mathrm{CH_3CHO}]^2$ with k = 6.73 × 10^{-6} $M^{-1}s^{-1}$

Exercise 6.4.4

rate = $k[\mathrm{OCl^-}]^2[I^-]$

k = 5.75×10^4 $M^{-2}s^{-1}$

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6.5: Integrated Rate Laws

Learning Objectives

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction by plotting concentration vs. time data according to expected reaction orders

The rate laws we have seen so far relate reaction rates to reactant concentrations. Using calculus, the rate law can be integrated to derive an equation that relates reactant concentration to time. This can be done for any reaction order, but in this chapter we will focus on the integrated rate laws for zero-, first-, and second-order reactions.

Using the integrated rate law equations we can:

- Determine how much reactant or product is present after a given time.
- Estimate how long a reaction takes to reach a certain extent.
- Determine the reaction order of a reactant by plotting the change in concentration over time using the expected linear relationships for zero-, first-, and second-order reactions

Zero-Order Integrated Rate Law

A zero-order reaction is one in which the reaction rate is independent of reactant concentration. This means that the reaction proceeds at a constant rate, regardless of how much reactant is present. The rate law for a zero-order reaction is:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^0 = k$$

CHM135 does not require you to use calculus on assessments. However, we will derive the integrated rate laws here so you understand where they come from, after that you can simply use them. As shown above, the rate of a zero order reaction is independent of concentration:

$$-\frac{d[A]}{dt} = k$$

This equation can be rearranged to:

$$d[A] = -k\,dt$$

By separating our variables and integrating our rate laws with respect $[A]$ on the left from $[A]_o$ to $[A]_t$ and with respect to t on the right from 0 to t,

$$\int_{[A]_o}^{[A]_t} d[A] = \int_0^t -k\,dt$$

we can generate the following linear relationships between concentration and time:

$$[A] - [A]_0 = -kt$$

This is the **integrated rate equation for a zero-order reaction**, but it is typically rearranged to the following format:

$$[A] = -kt + [A]_0$$

As it follows the general form of a linear equation:

$$y = mx + b$$

As shown in Figure $6.5.1$ the plot of concentration versus time for a zero-order reaction is a straight line with a slope of $-k$ and an intercept of $[A]_0$.

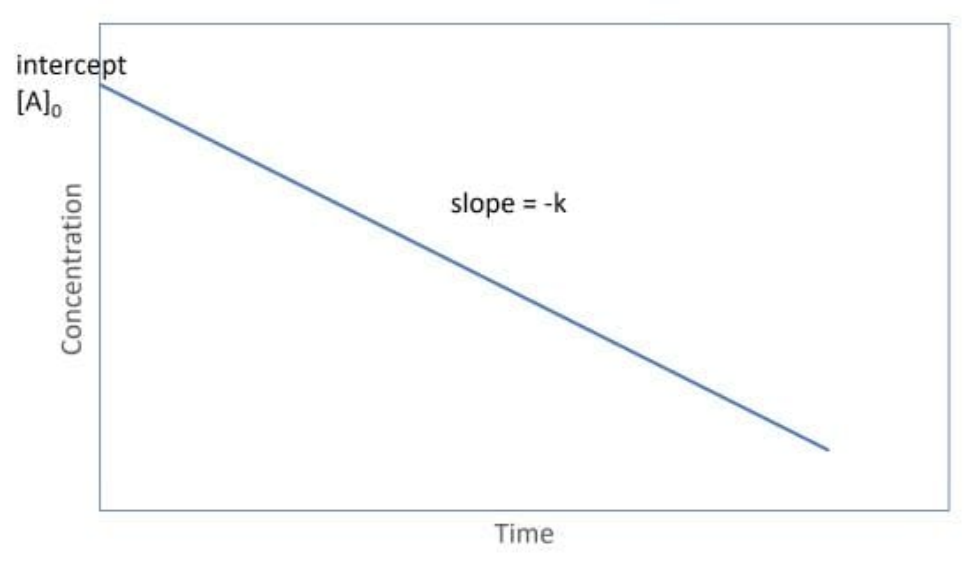


Figure $6.5.1$ shows a plot of concentration versus time for a zero order reaction.

If the reaction order is known to be zero then we can use the integrated rate equation above to calculate changes in concentration over time. If the reaction order is unknown we can test whether a reaction is zero-order by plotting concentration versus time as a reaction proceeds. If this gives a linear relationship then the reaction order for that reactant is zero. When we do this we are modeling the reaction as if it were zero-order and seeing how the data fits this model. If it's not linear then we need to explore another model (maybe first-order or second-order).

Figure $6.5.2$ shows an example of this approach where experimental data for the decomposition of ammonia ($\mathrm{NH_3}$) in the presence of two different materials at high temperatures are plotted together:

- Decomposition of ammonia ($\mathrm{NH_3}$) on tungsten (W)
- Decomposition of ammonia ($\mathrm{NH_3}$) on silica ($\mathrm{SiO_2}$)

From the plot of $[\mathrm{NH_3}]$ versus time we can see that the decomposition on tungsten gives a straight line while that on silica does not, indicating the reaction order for $\mathrm{NH_3}$ is zero when it involves tungsten but the reaction order of $\mathrm{NH_3}$ is not zero when it involves silica.

Having a reaction order of zero feels a bit strange, but this is not unusual when a reaction involves a solid catalyst, which is the case here. Ammonia gas diffuses onto the surface of the solid tungsten first and then once there they react. Once the surface is fully occupied, adding more ammonia does not increase the rate, leading to zero-order kinetics. From the slope of the line for the zero-order decomposition, the rate constant can be determined:

$$\text{slope} = -k = 1.3110^{-6}\,\mathrm{mol/L/s}$$

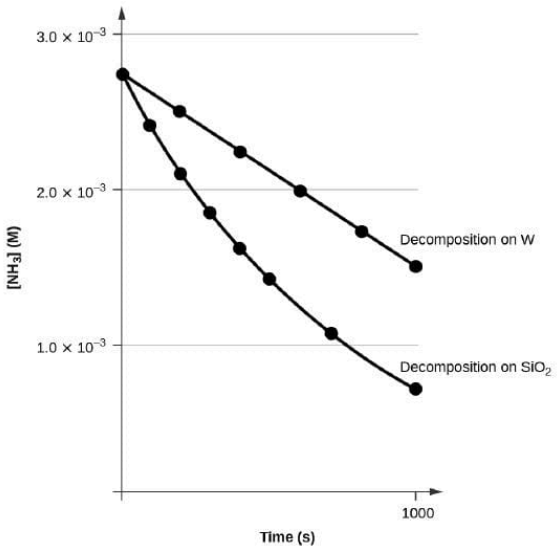


Figure 6.5.2: The decomposition of $\mathrm{NH_3}$ in the presence of tungsten (W) surface is a zero-order reaction, whereas, with quartz $(\mathrm{SiO_2})$, the reaction is first-order.

First-Order Integrated Rate Law

The rate law for a first-order reaction is:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^1$$

Changing deltas to differentials,

$$-\frac{d[A]}{dt} = k[A]$$

then rearranging the equation to separate the variables $[A]$ and t,

$$\frac{1}{[A]}d[A] = -k\,dt$$

we can integrate with respect to $[A]$ on the left from $[A]_o$ to $[A]_t$ and with respect to t on the right from 0 to t:

$$\int_{[A]_o}^{[A]_t} \frac{1}{[A]}\,d[A] = \int_0^t -k\,dt$$

This gives us the first-order integrated rate law, which provides a linear expression for changes in reactant concentration as a function of time,

$$ln[A] - \ln[A]_0 = -kt$$

or,

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

which can be rearranged into the form of a linear equation:

$$ln[A] = -kt + \ln[A]_0$$

$$y = mx + b$$

This is the **integrated rate expression for a first-order reaction**, and, similar to the zero-order reactions in the section above, this equation allows us to calculate the concentration of A at any time ($[A]_t$), given the initial concentration ($[A]_0$), the rate constant (k) and the elapsed time (t).

For a first-order reaction, a plot of $ln[A]$ versus t yields a straight line with a slope of $-k$ and an intercept of $ln[A]_0$. If data plotted this way does not result in a straight line, the reaction is not first order in A.

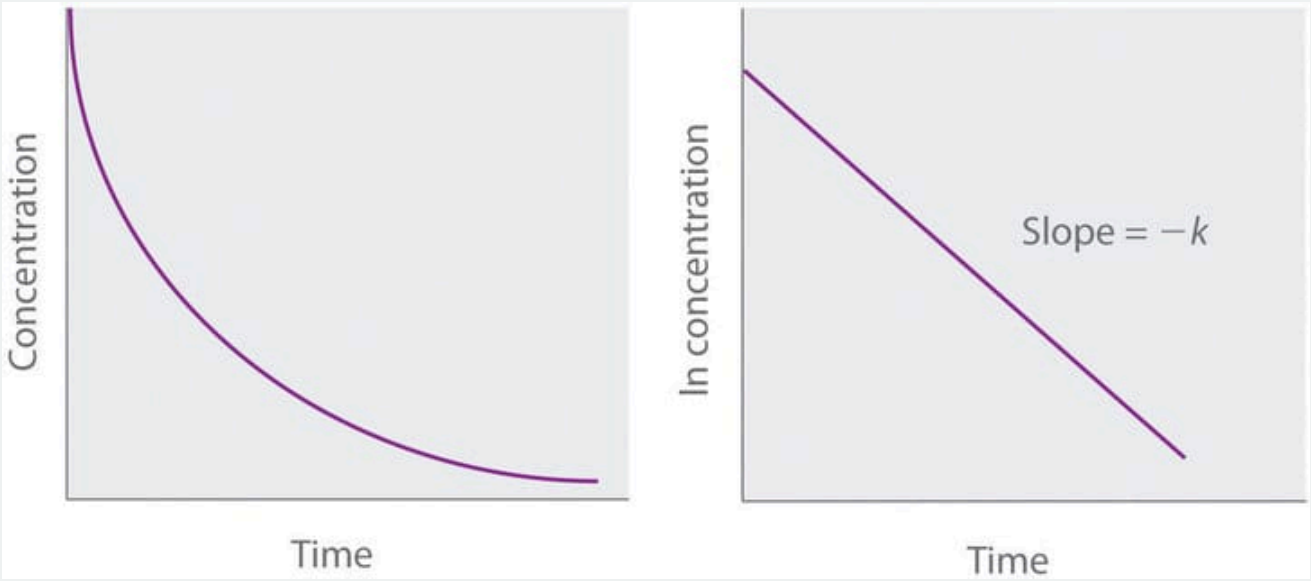


Figure 6.5.3: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (left) and the natural logarithm of reactant concentration versus time (right) for a first-order reaction.

Example 6.5.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is 9.2×10^{-3} s^{-1}:

$$C_4H_8 \longrightarrow 2\,C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

Since we need to find time, we use the integrated form of the rate law :

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

The initial concentration of C_4H_8, $[A]_0$, is not provided, we know that 80.0% of the sample has decomposed, meaning that 20.0% remains:

$[A]_t = 0.200[A]_0$

Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$
\begin{aligned}
t &= \ln \frac{[A]_0}{[0.200[A]_0]} \times \frac{1}{k} \\
&= \ln \frac{1}{0.200} \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\
&= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\
&= 1.7 \times 10^{2}\ \text{s}
\end{aligned}
$$

Exercise 6.5.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. All radioactive decay is first order. How many days will it take for 90% of the iodine–131 in a 0.500 *M* solution of this substance to decay to xenon-131?

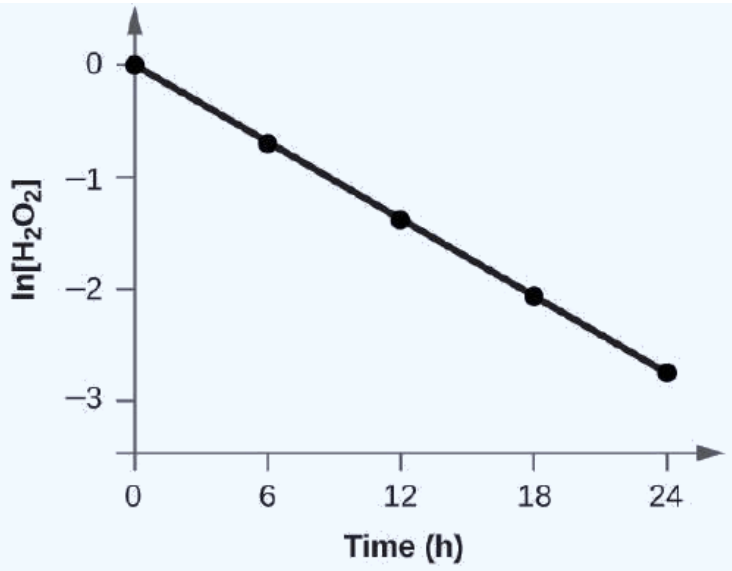
Answer available at the end of this section.

Example 6.5.2: Determination of Reaction Order by Graphing

Demonstrate that the decomposition of H_2O_2 follows a first-order rate law by graphing ln[H_2O_2] versus time. Determine the rate constant for the rate of decomposition of H_2O_2.

Time (h)	[H_2O_2] (*M*)	ln[H_2O_2]
0	>1.000	0.0
6.00	0.500	−0.693
12.00	0.250	−1.386
18.00	0.125	−2.079
24.00	0.0625	−2.772

Solution



The linear relationship between the $\ln[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

The rate constant for a first-order reaction is equal to the negative of the slope of the plot of $\ln[H_2O_2]$ versus time where:

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[H_2O_2]}{\Delta t}$$

To determine the slope of the line, we need two values of $\ln[H_2O_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when t is 6.00 h is –0.693; the value when t = 12.00 h is –1.386:

$$\begin{aligned}\text{slope} &= \frac{-1.386 - (-0.693)}{12.00\ \text{h} - 6.00\ \text{h}} \\ &= \frac{-0.693}{6.00\ \text{h}} \\ &= -1.155 \times 10^{-2}\ \text{h}^{-1} \\ k &= -\text{slope} = -(-1.155 \times 10^{-1}\ \text{h}^{-1}) = 1.155 \times 10^{-1}\ \text{h}^{-1}\end{aligned}$$

Exercise 6.5.2

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Data for the reaction $A \longrightarrow B + C$

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Answer available at the end of this section.

Second-Order Integrated Rate Law

A reaction that is second-order overall can occur in two ways:

- One reactant with a reaction order of 2: rate = k[A]^2
- Two reactants each with a reaction order of 1: rate = k[A][B]

In this section, we are focussing on the first case, which assesses whether the reaction order of a single reactant is second order. However, in the CHM135 laboratory we will explore how the reaction orders of multi-component rate laws can be determined.

The rate law for a second-order reaction is:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

Changing deltas to differentials,

$$-\frac{d[A]}{dt} = k[A]^2$$

then rearranging the equation to separate the variables $[A]$ and t,

$$\frac{1}{[A]^2}\, d[A] = -k\, dt$$

we can integrate with respect to $[A]$ on the left from $[A]_o$ to $[A]_t$ and with respect to t on the right from 0 to t:

$$\int_{[A]_o}^{[A]_t} \frac{1}{[A]^2}\, d[A] = \int_0^t -k\, dt$$

This gives us the second-order integrated rate law, which provides a linear expression for changes in reactant concentration as a function of time:

$$-\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = -kt \tag{6.5.1}$$

The **integrated rate law for the second-order reaction** can be rewritten in the form of a linear equation:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$
$$y = mx + b$$

For a second-order reaction, a plot of $\frac{1}{[A]}$ versus t yields a straight line with a slope of k and an intercept of $\frac{1}{[A]_0}$. If this plot is not a straight line, the reaction is not second order.

Example 6.5.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:

$$2\,C_4H_6(g) \longrightarrow C_8H_{12}\,(g)$$

The reaction is second order with a rate constant equal to 5.76 × 10^{-2} L/mol/min under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration remaining after 10.0 min?

Solution

We use the integrated form of the rate law to answer questions regarding time. For a second-order reaction, we have:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{[A]} = (5.76 \times 10^{-2}\ \text{L mol}^{-1}\ \text{min}^{-1})(10\ \text{min}) + \frac{1}{0.200\ \text{M}}$$

$$\frac{1}{[A]} = (5.76 \times 10^{-1}\ \text{M}^{-1}) + 5.00\ \text{M}^{-1}$$

$$\frac{1}{[A]} = 5.58\ \text{M}^{-1}$$

$$[A] = 1.79 \times 10^{-1}\ \text{M}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Exercise 6.5.3

Using the reaction in Example 6.5.4 with an initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer available at the end of this section.

Example 6.5.4: Determination of Reaction Order by Graphing

Test the data given to show whether the dimerization of C_4H_6 is a first- or a second-order reaction.

Solution

Solutions to Example 12.4.4

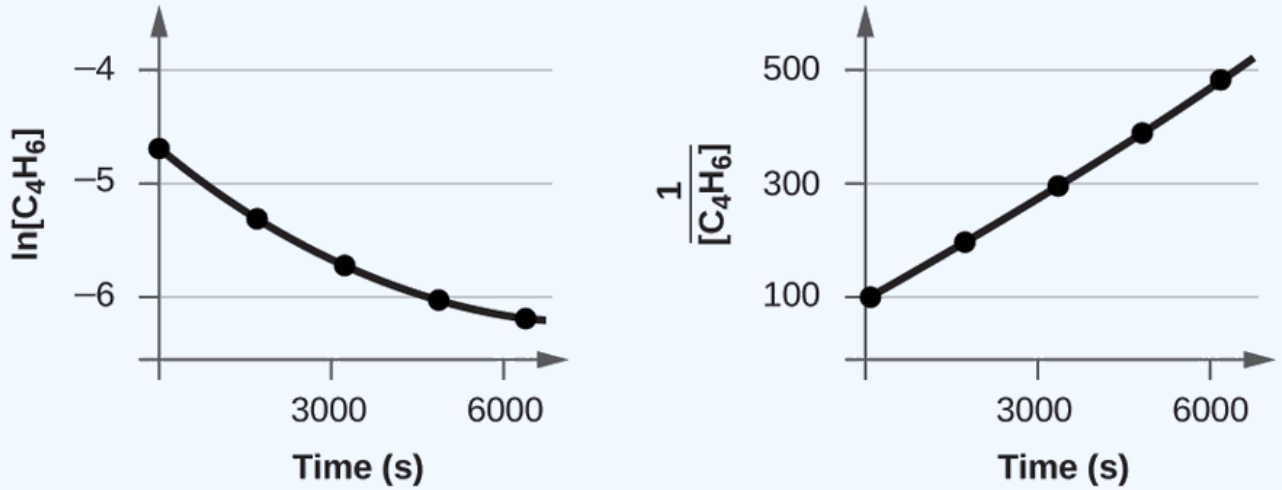
Time (s)	$[C_4H_6]$ (*M*)
0	1.00×10^{-2}
1600	5.04×10^{-3}
3200	3.37×10^{-3}
4800	2.53×10^{-3}
6200	2.08×10^{-3}

To distinguish a first-order reaction from a second-order reaction, we plot $\ln[C_4H_6]$ versus *t* and compare it with a plot of $\frac{1}{[C_4H_6]}$ versus *t*. The values needed for these plots follow.

Time (s)	$\frac{1}{[C_4H_6]}$ (M^{-1})	$\ln[C_4H_6]$
0	100	−4.605
1600	198	−5.289
3200	296	−5.692
4800	395	−5.978

Time (s)	$\frac{1}{[C_4H_6]}\ (M^{-1})$	ln[C_4H_6]
6200	481	−6.175

As you can see, the plot of ln[C_4H_6] versus *t* is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]}$ versus *t* is linear, indicating that the reaction is second order.



These two graphs show first- and second-order plots for the dimerization of C_4H_6. Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

Exercise 6.5.4

Does the following data fit a second-order rate law?

Data for second-order rate law

Trial	Time (s)	[*A*] (*M*)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Answer available at the end of this section.

The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for the reactant concentration to decrease by half. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. For a first-order reaction, the half-life remains constant and does not depend on the starting concentration.

For example, the decomposition of hydrogen peroxide (H_2O_2) follows first-order kinetics. Figure 6.5.4 shows its concentration

decreasing over time in a series of four half-lives:

- First half-life: $[H_2O_2]$ decreases from 1.00 M to 0.500 M
- Second half-life: $[H_2O_2]$ decreases from 0.500 M to 0.250 M
- Third half-life: $[H_2O_2]$ decreases from 0.250 M to 0.125 M
- Fourth half-life: $[H_2O_2]$ decreases from 0.125 M to 0.0625 M

From this plot, we can see that each half-life is 6 hours, confirming that the half-life of a first-order reaction remains constant over time.

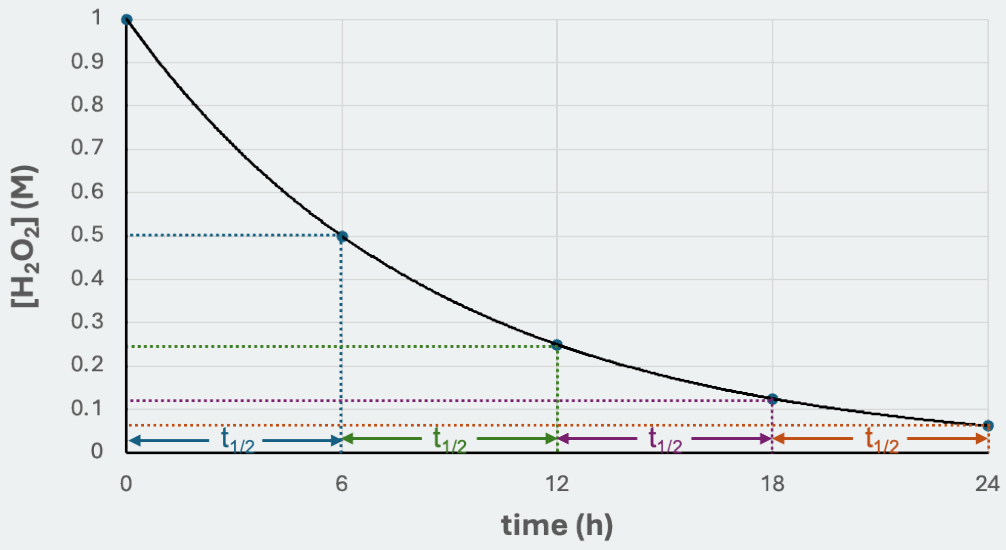


Figure 6.5.4: The decomposition of H_2O_2 is a first-order reaction. At a particular temperature, the half-life of the reaction is 6 hours, meaning that half of the H_2O_2 decomposes every 6 hours. This plot shows 4 successive half-lives where the $[H_2O_2]$ decreases from 1 M to 0.5 M in the first, 0.500 M to 0.250 M in the second, 0.250 M to 0.125 M in the third and 0.125 M to 0.0625 M in the fourth.

The half-life of a first-order reaction can be derived from its integrated rate law:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

Solving for t:

$$t = \frac{ln \frac{[A]_0}{[A]_t}}{k}$$

Since half-life is the time when [A] is half of its initial value, we substitute $[A]_t = 1/2[A]_0$ and set $t = t_{1/2}$:

$$t_{1/2} = \frac{ln \frac{[A]_0}{\frac{1}{2}[A]_0}}{k}$$

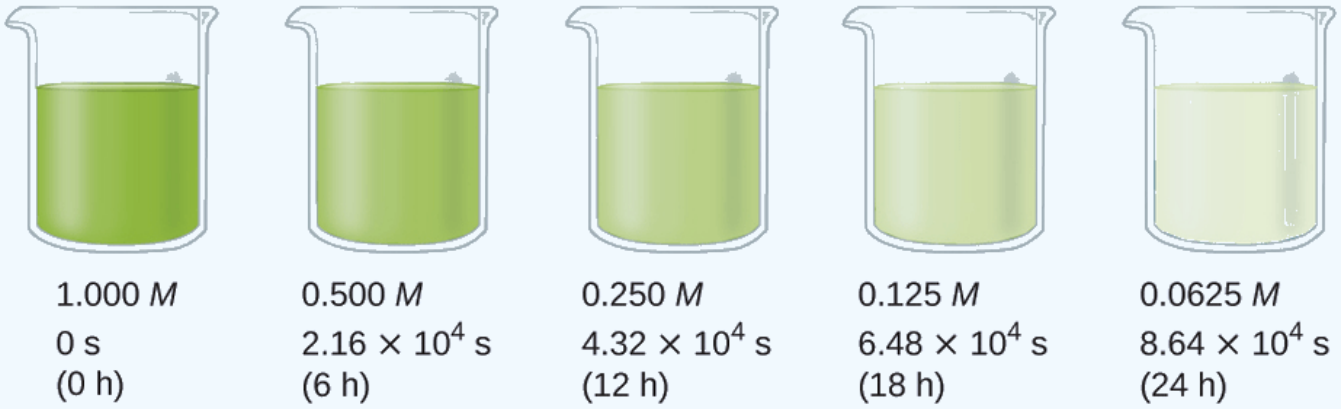
Simplifying:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

This equation shows that the half-life of a first-order reaction is independent of reactant concentration and depends only on the rate constant k. We can also see that the half-life of a first-order reaction is inversely proportional to the rate constant k. A fast reaction (larger k) will have a shorter half-life; a slow reaction (smaller k) will have a longer half-life. This relationship makes half-life calculations particularly useful in fields like pharmacology (drug metabolism) and nuclear chemistry (radioactive decay), where processes are often first-order and knowing how long a substance persists is essential.

Example 6.5.5: Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given below:



The decomposition of $\mathrm{H_2O_2}$ ($2\,\mathrm{H_2O_2} \longrightarrow 2\,\mathrm{H_2O} + \mathrm{O_2}$) at 40 °C is illustrated. The intensity of the colour symbolizes the concentration of $\mathrm{H_2O_2}$ at the indicated times; $\mathrm{H_2O_2}$ is actually colourless.

Solution

The half-life for the decomposition of $\mathrm{H_2O_2}$ is 2.16 × 10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4\ \mathrm{s}} = 3.21 \times 10^{-5}\ \mathrm{s^{-1}}$$

Exercise 6.5.5

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer available at the end of this section.

The half-life ($t_{1/2}$) of a zero-order reaction can be determined using the zero-order integrated rate law:

$$[A] = -kt + [A]_0$$

Substituting $t = t_{1/2}$ and $[A]_t = 1/2[A]_0$:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

This equation demonstrates that the half-life of a zero-order reaction depends on the initial concentration ($[A]_0$) and that as the reaction proceeds, the half-life decreases. This might seem strange, if the half-life is decreases... does that mean the rate of the reaction is increasing as time going on? No, that is (obviously) possible. In a zero-order reaction the rate of the reaction is unchanged with reactant concentration and so as the reaction proceeds the half-life gets shorter because there is simply less material present and so it will not take as long to half that smaller amount as the rate is not changing.

The half-life ($t_{1/2}$) of a second-order reaction can be determined using the second-order integrated rate law:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Substituting $t = t_{1/2}$ and $[A]_t = 1/2[A]_0$:

$$\begin{aligned}
\frac{1}{[A]} - \frac{1}{[A]_0} &= kt \\
\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\
\frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\
\frac{1}{[A]_0} &= kt_{1/2} \\
t_{1/2} &= \frac{1}{k[A]_0}
\end{aligned}$$

This equation shows that the half-life of a second-order reaction is inversely proportional to the initial concentration ($[A]_0$) and so as the reaction proceeds, the half-life increases. This increase in half-life means the reaction is proceeding at a slower rate as the reactant is consumed.

Comparing Zero-, First-, and Second-Order Reactions

The following table summarizes the key differences between zero-, first-, and second-order reactions:

Table 6.5.1: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Units of k	$M\ s^{-1}$	s^{-1}	$M^{-1}\ s^{-1}$
Integrated rate law	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \left(\frac{1}{[A]_0}\right)$
Graph for linear fit	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
Slope in graph	k = −slope	k = −slope	k = +slope
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Summary

Rate laws describe how the rate of a reaction depends on reactant concentration. Reaction orders and the rate constant within the rate law can be determined using the method of initial rates or graphical analysis of concentration vs. time data.

Integrated rate laws describe how reactant concentrations change over time and are derived by integrating the rate laws.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. In a zero-order reaction, the half-life decreases as the reaction proceeds. In a first-order reaction, the half-life is constant and does not depend on concentration. In a second-order reaction, the half-life increases as the reaction proceeds.

Glossary

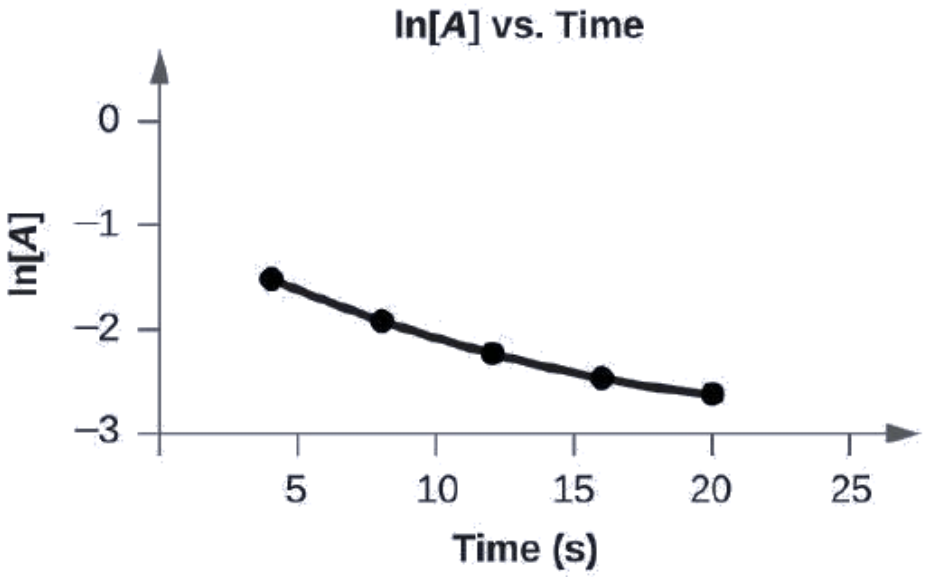
half-life of a reaction ($t_{1/2}$)
The time required for half of a given amount of reactant to be consumed.

integrated rate law
An equation that relates the concentration of a reactant to elapsed time of reaction.

Answers

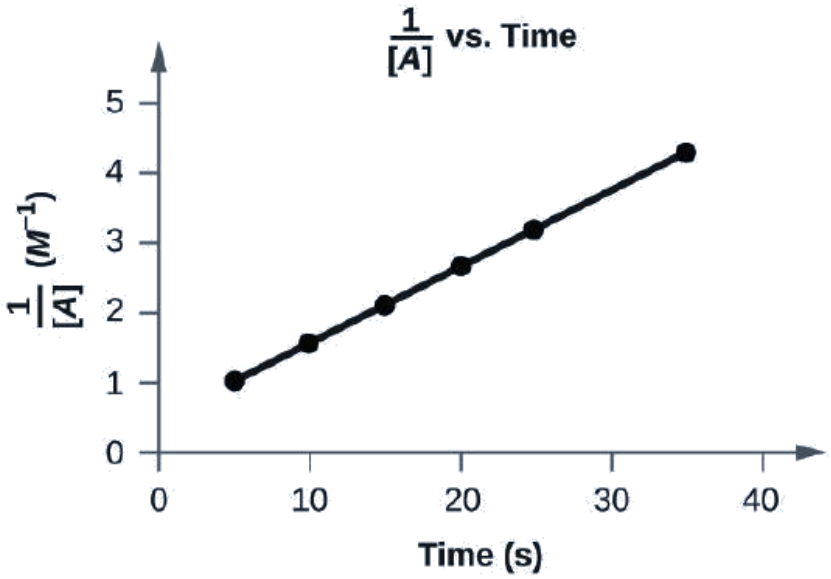
Exercise 6.5.1
16.7 days

Exercise 6.5.2
The plot of ln[A] vs. t is not a straight line. The equation is not first order:



Exercise 6.5.3
0.0195 mol/L

Exercise 6.5.4
Yes. The plot of $\frac{1}{[A]}$ vs. t is linear:



Exercise 6.5.5

5.02 d.

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6.6: Collision Theory, Activation Energy, and the Arrhenius Equation

Learning Objectives

- Define the concepts of activation energy and transition state
- Explain the dependence of rate on concentration and temperature using collision theory
- Relate the temperature, activation energy, and rate constant through the Arrhenius equation

For a chemical reaction to occur, reactant atoms, molecules, or ions must collide. Since atoms must be close together to form chemical bonds, the frequency and nature of these collisions determine reaction rates. Collision theory explains how molecular collisions lead to reactions and why some reactions occur faster than others.

Postulates of Collision theory

1. The rate of a reaction is proportional to the rate of reactant collisions:
$$\text{reaction rate} \propto \frac{\#\,\text{collisions}}{\text{time}}$$
2. Molecules must collide with the correct orientation so that the atoms involved in bond formation make contact.
3. Collisions must have enough energy to break existing bonds and form new ones. This minimum energy requirement is called the activation energy (E_a).

Consider the reaction of carbon monoxide, a pollutant produced from the combustion of fuels, with oxygen:

$$2\,\mathrm{CO}(g)+\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g)$$

This reaction is crucial for reducing carbon monoxide emissions from vehicles. The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$\mathrm{CO}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{O}(g)$$

However, not all collisions between CO and $\mathrm{O_2}$ molecules lead to products. Molecules can collide in many different orientations, but only certain alignments allow the reaction to occur. Figure $6.6.1$ shows just two possibilities:

- If the oxygen end of the CO molecule collides with $\mathrm{O_2}$, the reaction is unlikely because the carbon and oxygen atoms needed to form $\mathrm{CO_2}$ are not properly aligned.
- If the carbon end of the CO molecule collides with $\mathrm{O_2}$, the reaction is more likely to proceed, forming carbon dioxide ($\mathrm{O{=}C{=}O}$).

If the oxygen end of the CO molecule collides with $\mathrm{O_2}$ (first case), the reaction is unlikely to occur because the carbon and oxygen atoms needed to form $\mathrm{CO_2}$ line up. The second case is more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms ($\mathrm{O{=}C{=}O}$). This example demonstrates how molecular orientation is a factor in determining whether a collision is successful.

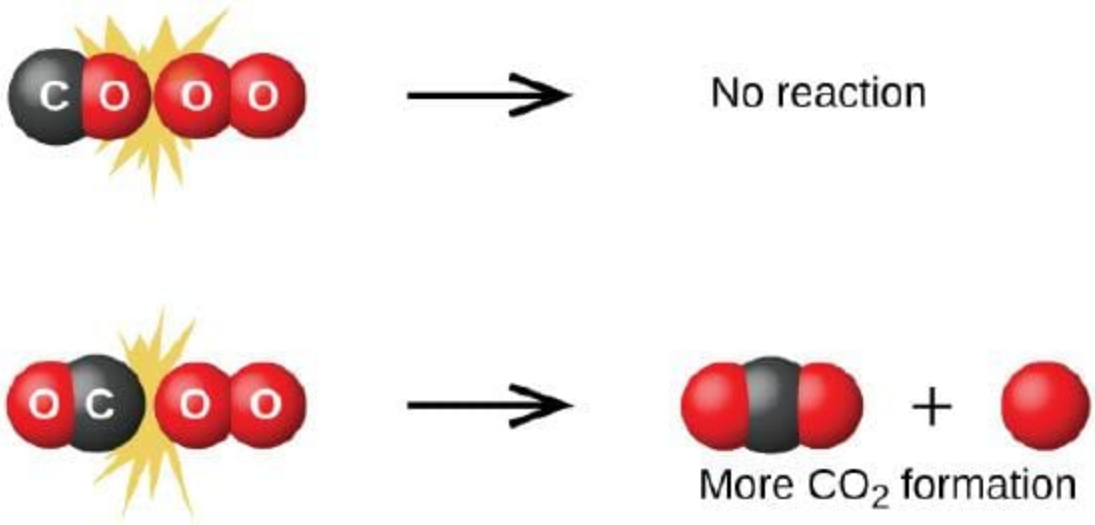


Figure 6.6.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

Not all collisions with the correct orientation result in the formation of products. Collisions must also occur with sufficient energy for the reaction to take place. This minimum required energy is called the activation energy (E_a). Reactant molecules must collide with enough energy to reach a transition state, a high-energy intermediate in which bonds are partially broken and formed. We will explore activation energies and transition states further in the next section.

Collision theory also explains how reaction rates depend on concentration. When the concentration of a reactant increases, the number of molecular collisions per unit time also increases. More collisions lead to a faster reaction rate, provided that the colliding molecules have enough energy to overcome the activation barrier.

Activation Energy

The activation energy, E_a, is the minimum energy required for a reaction to occur. Figure 6.6.2 shows the energy profile for a general reaction:

$$A + B \longrightarrow C + D$$

The activation energy for the forward reaction is the energy difference between the reactants and the transition state, a high-energy intermediate.

As reactants approach each other, their kinetic energy is converted into potential energy as they reach the transition state. If the reactants do not have sufficient energy to reach the transition state products will not form, reactants A and B will reform and potential energy will be transformed back into kinetic energy.

If A and B collide with sufficient energy to reach the transition state it can transform back into reactants A and B or into products C and D. The transition state is the highest energy species between reactants and products and so it represents the energy barrier required to transform reactants into products but forward progress is not guaranteed and the observed rate of reaction includes the probability of the transition state transforming back to reactants or forward towards products. If the transition state proceeds towards products, the potential energy of the transition state is converted to chemical energy of the bonds formed and broken as well as the resulting kinetic energy of the products.

The chemical energy stored in the bonds of the products is not always the same as that of the reactants and ΔH represents the energy difference between the potential energies of the reactants (A and B) and the products (C and D). If the products have a lower potential energy than the reactants this energy will be transferred to the products as kinetic energy, which will be transferred to surrounding molecules, increasing their overall average kinetic energy or temperature. This is an example of an exothermic reaction, and is what is represented in Figure 6.6.2. Conversely, if the products have a higher potential energy than the reactants they will receive less kinetic energy, which will decrease the overall kinetic energy of the surrounding molecules, decreasing the temperature. This is an endothermic reaction.

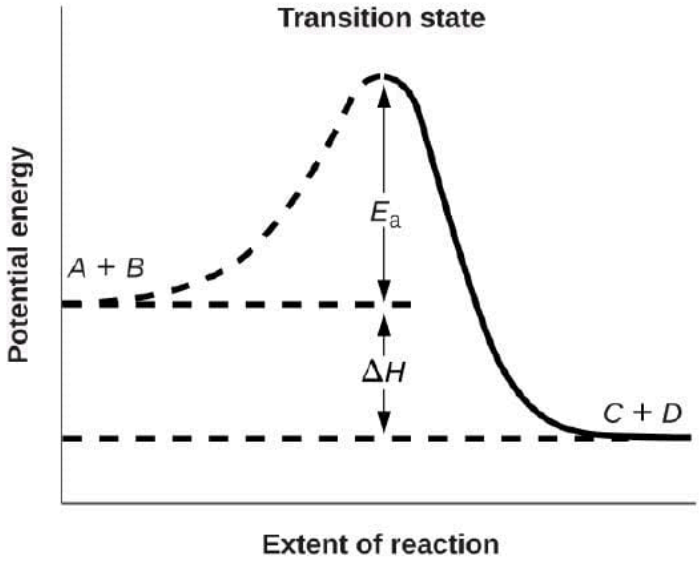


Figure 6.6.2: This graph shows the potential energy relationships for the reaction $A + B \longrightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of C and a molecule of D present. The activation energy for the forward reaction is represented by E_a. The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH. The peak represents the transition state.

Reactions with lower activation energies occur more quickly. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will be slow because only a small fraction of molecules will have enough energy to react. Conversely, if the activation energy is much smaller than the average kinetic energy, a greater fraction of molecules will possess the necessary energy, leading to frequent successful collisions and a faster reaction.

You previously encountered kinetic molecular theory (KMT) when studying gases. According to KMT, molecules in a sample have a range of kinetic energies, rather than a single fixed energy. At a given temperature, only a fraction of molecules have kinetic energy greater than the activation energy (E_a).

The relationship between activation energy and temperature on the fraction of molecules that can react is depicted visually in Figure 6.6.3:

- At a given temperature, a reaction with a lower activation energy will result in a larger fraction of molecules with enough energy to react. In Figure 6.6.3(a) the opaque shaded area indicates the number of molecules with sufficient kinetic energy to react via the higher activation energy (E_a) reaction and this extends to include both the hatched and opaque shaded areas for a lower E_a reaction.
- Increasing temperature ($T_2 > T_1$) shifts the kinetic energy distribution so that more molecules have sufficient kinetic energy to exceed E_a. In Figure 6.6.3(b) the number of molecules with sufficient energy to react increases from T_1 (opaque shaded area) to T_2 (hatched and opaque shaded areas). This explains why higher temperatures typically lead to faster reaction rates.

In everyday life, we know that food stored in a refrigerator lasts longer than food left at room temperature. This is because the lower temperature reduces the fraction of molecules with enough energy to react, slowing spoilage reactions. Similarly, cold-blooded animals (such as reptiles and insects) move more slowly on cold days because the biochemical reactions that power their muscles occur more slowly at lower temperatures.

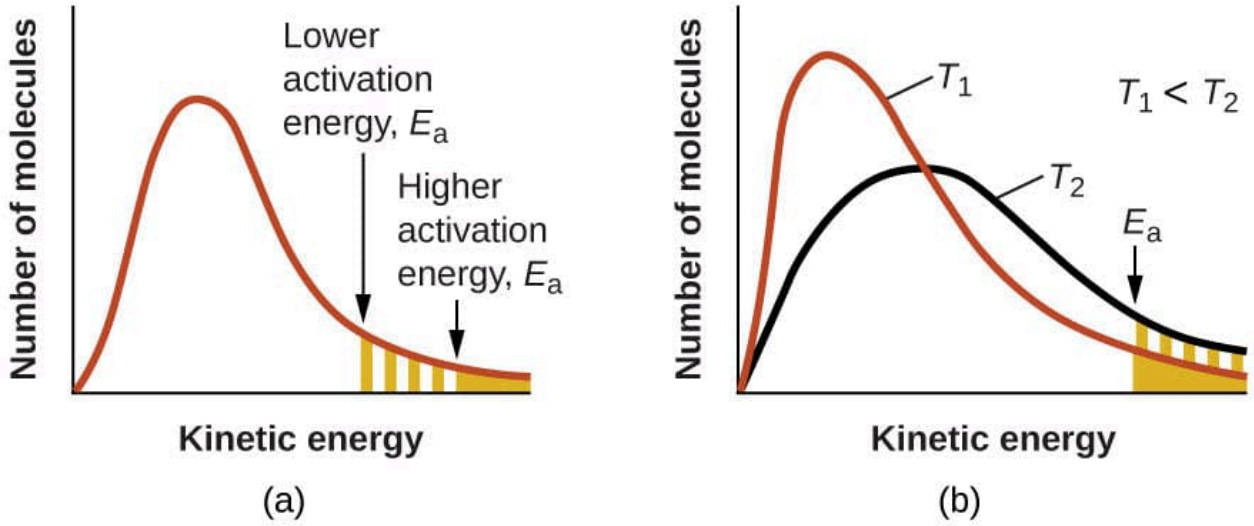


Figure 6.6.3: (a) As the activation energy of a reaction decreases, more molecules have this minimum energy, as shown by the shaded areas. (b) At a higher temperature, T2, more molecules have kinetic energies greater than Ea, as shown by the yellow shaded area.

Let's look at a reaction energy diagram in more detail. Consider the following reaction:

$$\mathrm{CH_3Br + OH^- \longrightarrow CH_3OH + Br^-}$$

Figure 6.6.4 illustrates the change in potential energy as the reaction progresses from reactants to products. Since this reaction is exothermic, the products are lower in energy than the reactants. This also means that the activation energy for the forward reaction is lower than that for the reverse reaction.

As the reactants approach each other, repulsion between their electron clouds increases, causing kinetic energy to convert into potential energy, which slows their movement. If the collision occurs with sufficient energy, the reactants can reach the transition state, a high-energy, unstable species with partially broken and formed bonds.

In this reaction, the transition state consists of the central carbon atom surrounded by five other atoms. The carbon atom has three bonds to hydrogen atoms, a partial bond to bromine that is weakening, and a partial bond to oxygen that is forming. From the transition state, the reaction can proceed in either direction, towards products or back towards reactants.

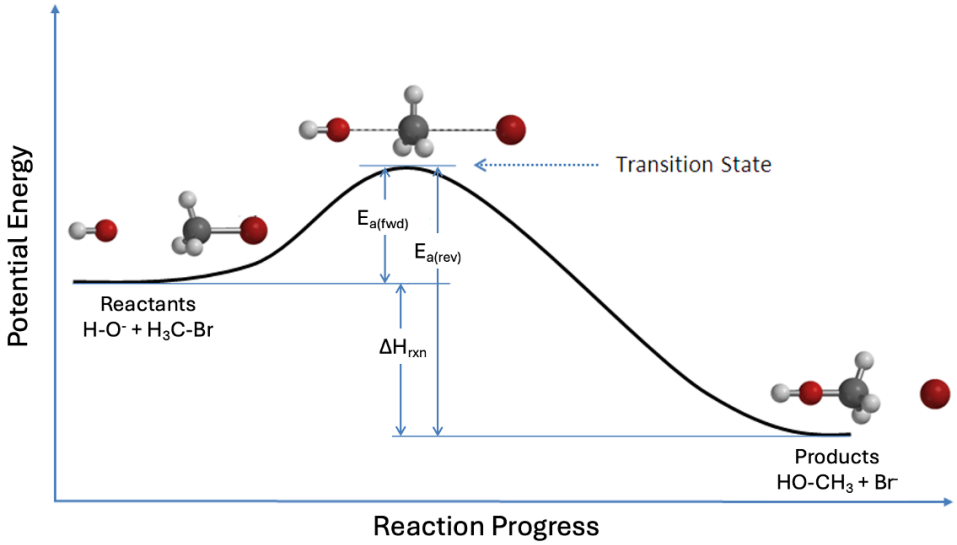


Figure 6.6.4: Energy Profile of the reaction $\mathrm{CH_3Br + OH^- \longrightarrow CH_3OH + Br^-}$. (Copyright; author via source Transition state theory. (2024, October 21). In *Wikipedia*. https://en.wikipedia.org/wiki/Transition_state_theory)

The Arrhenius Equation

The Arrhenius equation allows us to quantify the relationship between activation energy (E_a) and the rate constant (*k*) for a reaction:

$$k = Ae^{-E_a/RT} \tag{6.6.1}$$

where:

- R = universal gas constant (8.314 J mol^{-1} K^{-1})
- T = temperature (K)
- E_a = activation energy (J mol^{-1})
- A = frequency factor, a constant related to the frequency of collisions and their orientation (same units as *k*)

The Arrhenius equation relates the rate constant of a reaction (*k*) with the two key ideas of collision theory:

- The frequency factor (A) accounts for the number of collisions with the correct orientation.
- The exponential term $e^{-E_a/RT}$ represents the fraction of molecules with enough kinetic energy to overcome the activation energy barrier.

The Arrhenius equation describes quantitatively much of what we have already discussed about reaction rates:

- **Relationship between activation energy (E_a) and reaction rate:** For two reactions at the same temperature, a larger E_a results in a smaller value of $e^{-E_a/RT}$, meaning fewer molecules have sufficient kinetic energy to react, resulting in a smaller rate constant (*k*) and a slower reaction rate. Conversely, a reaction with a smaller E_a has a larger fraction of molecules with sufficient energy, leading to a higher *k* and a faster reaction rate.
- **Relationship between temperature (T) and reaction rate:** Increasing temperature (T) results in a larger value of $e^{-E_a/RT}$, meaning more molecules have sufficient kinetic energy to react, resulting in a larger rate constant (*k*) and a faster reaction rate.

As it connects the rate constant (*k*) of a reaction with temperature (T) and activation energy (E_a), the Arrhenius equation can be used to determine the activation energy barrier of a reaction by measuring the rate constant at different temperatures. This is

simplified by taking the natural logarithm of both sides of the Arrhenius equation to produce a linear relationship:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$
$$y = mx + b$$

Plotting $\ln k$ versus $\frac{1}{T}$ produces a straight line. The slope of this line is $\frac{-E_a}{R}$, from which E_a may be determined. The y-intercept gives the value of $\ln A$.

Example 6.6.1

The table below provides rate constant (k) values at different temperatures for the decomposition of $\mathrm{HI}(g)$ into $\mathrm{H_2}(g)$ and $\mathrm{I_2}(g)$. Determine the activation energy (E_a) for this reaction.

$$2\,\mathrm{HI}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{I_2}(g)$$

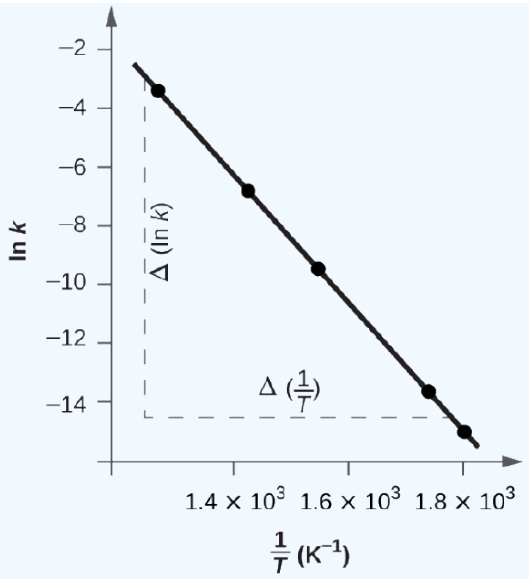
T (K)	k ($M^{-1}s^{-1}$)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Values of $\frac{1}{T}$ and ln k are:

$\frac{1}{T}$ (K^{-1})	ln k
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Below is a graph of ln k versus $\frac{1}{T}$. To determine the slope of the line, we need two values of ln k, which are determined from the line at two values of $\frac{1}{T}$ (one near each end of the line is preferable). For example, the value of ln k determined from the line when $\frac{1}{T} = 1.25 \times 10^{-3}$ is −2.593; the value when $\frac{1}{T} = 1.78 \times 10^{-3}$ is −14.447.



This graph shows the linear relationship between $\ln k$ and $\frac{1}{T}$ for the reaction $2\,\mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I_2}$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

$$\begin{aligned}\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3}\,\mathrm{K^{-1}}) - (1.25 \times 10^{-3}\,\mathrm{K^{-1}})} \\ &= \frac{-11.854}{0.53 \times 10^{-3}\,\mathrm{K^{-1}}} = 2.2 \times 10^{4}\,\mathrm{K} \\ &= -\frac{E_\mathrm{a}}{R}\end{aligned}$$

Thus:

$$\begin{aligned}E_\mathrm{a} &= -\text{slope} \times R = -(-2.2 \times 10^{4}\,\mathrm{K} \times 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}) \\ &= 1.8 \times 10^{5}\,\mathrm{J\,mol^{-1}}\end{aligned}$$

When only two temperature values and their corresponding rate constants are available, we can derive an equation that allows us to find the activation energy:

$$\ln k_1 = \left(\frac{-E_\mathrm{a}}{R}\right)\left(\frac{1}{T_1}\right) + \ln A$$

$$\ln k_2 = \left(\frac{-E_\mathrm{a}}{R}\right)\left(\frac{1}{T_2}\right) + \ln A$$

Subtracting these two equations eliminates lnA and gives:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_\mathrm{a}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{6.6.2}$$

To see an example calculation, let's use the first entry and the last entry from the previous example :

First and Last Entry

T (K)	k ($M^{-1}s^{-1}$)	$\frac{1}{T}$ (K^{-1})	ln k
555	3.52×10^{-7}	1.80×10^{-3}	−14.860
781	3.95×10^{-2}	1.28×10^{-3}	−3.231

$$\ln\left(\frac{3.95 \times 10^{-2} M^{-1}s^{-1}}{3.52 \times 10^{-7} M^{-1}s^{-1}}\right) = \frac{-E_a}{8.314 \frac{J}{mol \cdot K}}\left(\frac{1}{781K} - \frac{1}{555K}\right)$$

$$11.63 = 6.27 \times 10^{-5} \frac{mol}{J} E_a$$

$$E_a = 1.85 \times 10^5 J/mol \text{ or } 185 kJ/mol$$

This method is particularly useful when only a limited number of temperature-dependent rate constants are available for a reaction.

Exercise 6.6.1

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 $M^{-1}s^{-1}$ at 650 K and 7.39 $M^{-1}s^{-1}$ at 700 K:

$$2\,N_2O_5(g) \longrightarrow 4\,NO(g) + 3\,O_2(g)$$

Calculate the activation energy for this decomposition.

Answer available at the end of this section.

Summary

Collision theory states that reactant molecules must collide with the correct orientation and sufficient energy to react. The activation energy is the minimum energy needed to reach the transition state, an unstable species between reactants and products with bonds partially broken and formed. The rate of a reaction is characterized by its rate constant, *k*, which is related to the activation energy barrier of the reaction, the temperature at which the reaction takes place, and the proportion of effective collisions.

Reaction energy diagrams illustrate how energy changes during a reaction. They visualize the energy of the transition state and the resulting activation energy barriers for both the forward and reverse reactions as well as the overall enthalpy change of the reaction.

The Arrhenius equation quantitatively describes how temperature and activation energy affect the rate constant. It allows the activation energy to be determined experimentally by measuring the rate constant at different temperatures.

Glossary

activation energy (E_a)
: The energy necessary in order for a reaction to take place.

Arrhenius equation
: The mathematical relationship between the rate constant and the activation energy of a reaction.

collision theory
: Model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics.

frequency factor (A)
: Proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation.

reaction energy diagram
: Diagram that illustrates how energy changes during a reaction, including the transition states, activation energy barriers, and overall enthalpy change.

Answers

Exercise 6.6.1

$$\ln\left(\frac{7.39\ M^{-1}s^{-1}}{1.66\ M^{-1}s^{-1}}\right) = \frac{-E_a}{8.314\frac{J}{mol\cdot K}}\left(\frac{1}{700\ K} - \frac{1}{650\ K}\right)$$

E_a = 113,000 J/mol

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6.7: Reaction Mechanisms

Learning Objectives

- Identify the molecularity of elementary reactions (unimolecular, bimolecular, or termolecular).
- Write balanced chemical equations for overall reactions given a reaction mechanism.
- Write rate laws for elementary reactions and derive rate laws for overall reactions, considering slow steps and equilibrium approximations.
- Identify reaction intermediates within multi-step mechanisms.
- Assess the validity of a proposed mechanism by comparing its derived rate law to experimental data.
- Interpret and draw potential energy diagrams to illustrate reaction mechanisms, including transition states and rate-determining steps.

Elementary Reactions

A balanced chemical equation tells us which substances react, which substances are produced, and how the amounts of reactants and products are related. However, it does not show *how* the reaction actually proceeds at the molecular level. Most chemical reactions occur through a sequence of simpler reactions. A reaction mechanism is a step-by-step series of simpler reactions by which an overall reaction takes place.

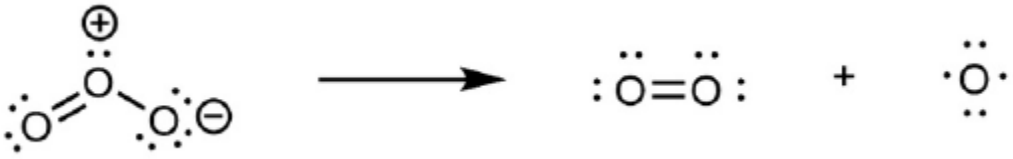
For example, ozone in the stratosphere protects Earth's surface from harmful ultraviolet radiation. Ultraviolet photons cause ozone molecules to decompose into oxygen molecules. The overall reaction equation is:

$$2\ \mathrm{O_3}(g) \xrightarrow{h\nu} 3\ \mathrm{O_2}(g)$$

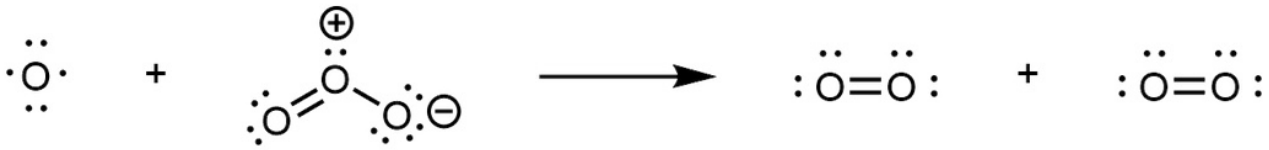
Although this equation indicates which substances are consumed and produced, it does not mean that two $\mathrm{O_3}$ molecules collide and react directly. Instead, the reaction proceeds in two consecutive steps:

$$\begin{aligned}
&\text{step 1:} && \mathrm{O_3}(g) && \xrightarrow{h\nu} && \mathrm{O_2}(g) + \mathrm{O}(g)\\
&\text{step 2:} && \mathrm{O}(g) + \mathrm{O_3}(g) && \longrightarrow && 2\ \mathrm{O_2}(g)\\
&\text{overall:} && 2\ \mathrm{O_3}(g) && \longrightarrow && 3\ \mathrm{O_2}(g)
\end{aligned}$$

Step 1 occurs when an $\mathrm{O_3}$ molecule absorbs a UV photon, breaking a bond and producing an $\mathrm{O_2}$ molecule and a free O atom:



Step 2 involves the newly formed O atom reacting with another $\mathrm{O_3}$ molecule to produce two $\mathrm{O_2}$ molecules:



Adding these steps together yields the overall reaction:

$$O_3(g) + \cancel{O(g)} + O_3(g) \rightarrow O_2(g) + \cancel{O(g)} + 2O_2(g)$$

which simplifies to the overall reaction equation: $2\,\mathrm{O_3\,(g)} \longrightarrow 3\,\mathrm{O_2\,(g)}$

A species such as O that appears as a product in one step but is consumed in a subsequent step is called a reaction intermediate. Intermediates are typically less stable than either the reactants or the products, but unlike transition states, they have fully formed bonds and can sometimes be isolated.

Each step in a mechanism is called an elementary reaction. An elementary reaction explicitly shows which particles collide, break apart, or rearrange to form the products and/or intermediates. For instance, step 2 above requires a collision between a single O atom and a single $\mathrm{O_3}$ molecule, which then forms two $\mathrm{O_2}$ molecules.

By contrast, the overall equation $2\,\mathrm{O_3\,(g)} \longrightarrow 3\,\mathrm{O_2\,(g)}$ does not imply a direct collision of two $\mathrm{O_3}$ molecules. Instead, the overall equation is simply the net result of multiple elementary steps.

Because each elementary reaction has its own transition state (an energy maximum), a multi-step mechanism will involve a series of transition states. Figure $6.7.1$ illustrates the reaction energy diagram for the ozone decomposition, showing two distinct peaks, each corresponding to a transition state.

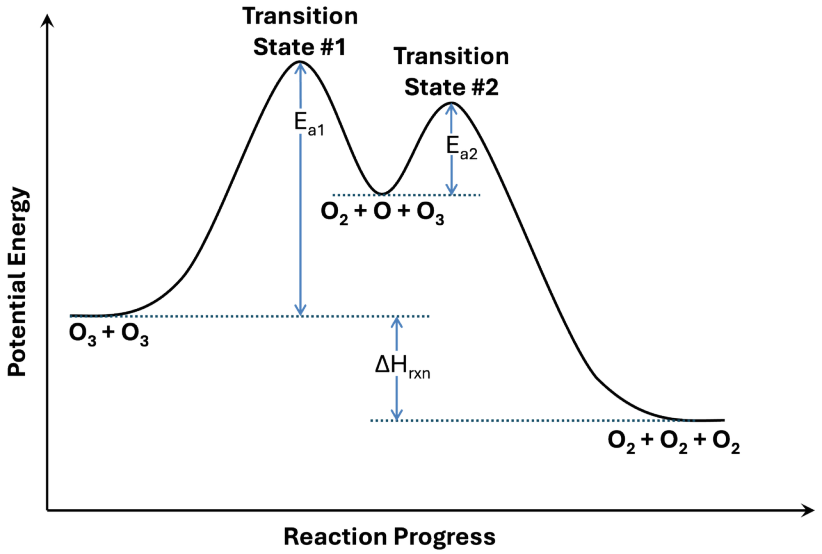


Figure $6.7.1$: Reaction energy diagram for the overall $2\,\mathrm{O_3\,(g)} \longrightarrow 3\,\mathrm{O_2\,(g)}$ reaction. This reaction proceeds via a mechanism consisting of two elementary reaction steps.

Even though one $\mathrm{O_3}$ molecule does not react until step 2, it is included among the reactants in the energy diagram from the start as it is required in the second step. In a reaction energy diagram, all atoms and molecules that participate in the reaction are accounted for from the beginning to the end of the process.

In previous chapters we have emphasized that reaction stoichiometry cannot be used to predict the reaction orders of a rate law. This is true for overall reactions, but because elementary reactions describe an actual molecular event we can use their stoicheiometry to determine the reaction orders of the accompanying rate law. We will discuss this in more detail throughout this chapter.

Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant particles (atoms, molecules, or ions) involved in that step. A

unimolecular elementary reaction involves the rearrangement or decomposition of a single reactant molecule, for example:

$$\text{A} \rightarrow \text{products}$$

At a given concentration of A ([A]) only a fraction of A molecules (those that can surpass the activation energy) will react at a given temperature. Doubling [A] doubles the number of A molecules capable of reacting, so the rate of the reaction doubles. Thus, for a unimolecular elementary reaction:

$$\text{rate} = k[\text{A}]$$

This means such a reaction is first-order overall. Because an elementary reaction directly represents the actual molecular event, we can determine its reaction order simply by looking at its stoichiometry.

A unimolecular reaction can be part of a more complex mechanism (as with the ozone decomposition, where, $\mathrm{O_3 \longrightarrow O_2 + O}$ is a unimolecular step), or it may represent the sole step in the reaction mechanism. In other words, an elementary reaction can also be an overall reaction.

Bimolecular Elementary Reactions

A bimolecular elementary reaction involves the collision of two reactant particles. The general forms are:

1. Collision between two different reactants:

   $\text{A} + \text{B} \rightarrow \text{products}$

   $\text{rate} = k[\text{A}][\text{B}]$

   This elementary step is first order in A and first order in B, making the reaction second-order overall.

2. Collision between two identical reactant molecules:

   $\text{A} + \text{A} \rightarrow \text{products}$ or $2\ \text{A} \rightarrow \text{products}$

   $\text{rate} = k[\text{A}]^2$

   This elementary step is second order in A and second-order overall.

Figure $6.7.2$ illustrates a reaction of the type A + B → products. It demonstrates that the collision frequency (and thus the reaction rate) doubles as the concentration of either reactant doubles. If both reactant concentrations double, the total number of collisions increases by a factor of four, consistent with a second-order rate law.

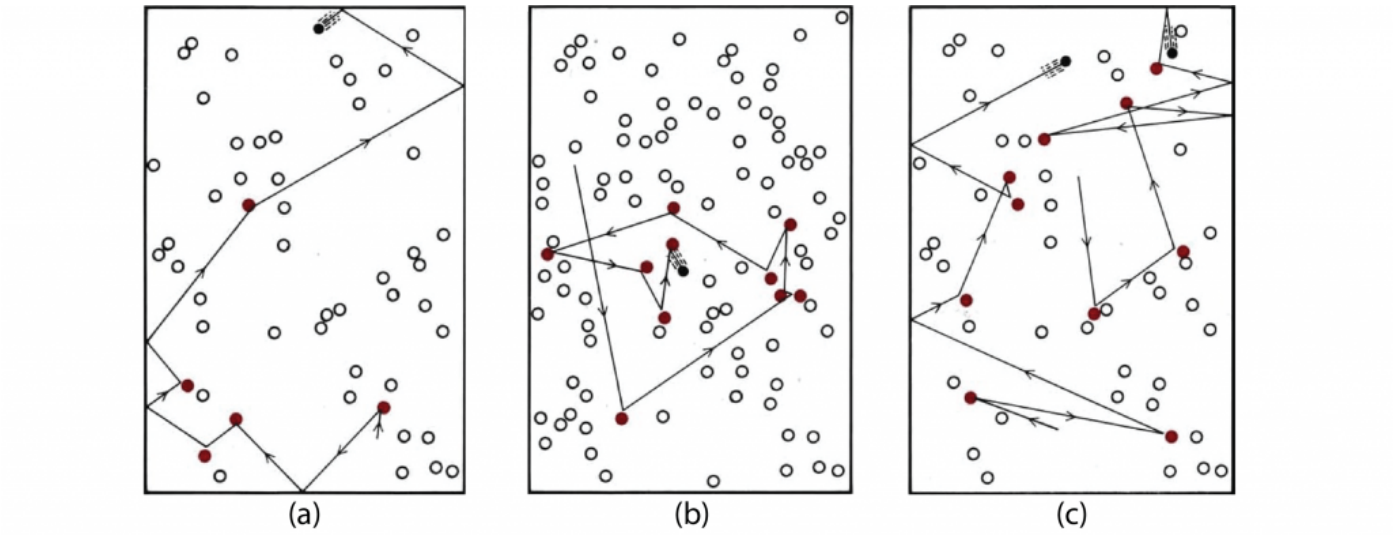


Figure 6.7.2 *The effect of concentration on the collision frequency for a bimolecular reaction. (a) A single black molecule moving among 50 white molecules collides with 5 white molecules in 1 s. (Each white molecule that has been struck by a moving black molecule is shown in color.) (b) Doubling the number of white molecules doubles the collision frequency to 10 collisions/s. (c) Having two black molecules moving among 50 white ones also yields 10 collisions/s. The collision rate is proportional to both the concentration of white molecules and the concentration of black molecules.*

These observations confirm that the collision rate—and thus the reaction rate—is proportional to the concentration of both reactants.

A real-world example of a bimolecular elementary reaction is Step 2 in the ozone decomposition mechanism discussed earlier:
$\mathrm{O\,(g) + O_3\,(g) \longrightarrow 2\,O_2\,(g)}$

Termolecular Elementary Reactions

A termolecular elementary reaction involves three reactant particles colliding simultaneously. Because the probability of three particles colliding at once is quite low, termolecular elementary reactions are rare (less than 0.1% of the probability of two particles colliding). More often, what appears to be a three-reactant reaction is actually a series of unimolecular and/or bimolecular steps. Nevertheless, a few established termolecular reactions exist. For instance, the oxidation of nitric oxide by oxygen appears to involve a termolecular step:

$$\mathrm{2\,NO + O_2 \longrightarrow 2\,NO_2}$$
$$\mathrm{rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

Relating Reaction Mechanisms to Rate Laws

A reaction mechanism consists of a series of elementary reactions and a valid mechanism for a multi-step reaction must meet the following criteria:

- It is composed of plausible elementary reactions (usually unimolecular or bimolecular).
- The sum of the elementary steps matches the overall balanced reaction.
- The mechanism agrees with the experimentally determined rate law.

For elementary reactions, rate laws can be written directly from the stoichiometric coefficients. However, the rate law of an overall multi-step reaction cannot be derived just by looking at the overall balanced equation. Instead, the overall rate law must be determined by combining the rate laws of the individual elementary steps in a way that reflects the reaction mechanism.

To evaluate a mechanism's validity, the theoretical rate law (derived from the mechanism) can be compared to the experimentally determined rate law. If the two agree, the proposed mechanism is consistent with experimental data and is a plausible

mechanism to describe how the reaction proceeds. Additional experimental evidence, such as the detection of a proposed intermediate, can further support a proposed mechanism.

When proposing a reaction mechanism it is also necessary to define the relative energetics of each step. These energetics do not need to be quantitative with proposed activation energies for each step, they simply need to identify which step in the mechanism is the slowest step, known as the rate-determining step. The rate determining step determines the overall reaction rate. Even if all other steps are faster, the reaction cannot proceed faster than its slowest step. This is analogous to a production line, where the speed of the entire process is limited by the slowest machine. In this way, the rate law of the overall reaction corresponds to the rate law of the rate-determining step.

The next two sections will take you through the derivation of rate laws from reaction mechanisms. First we will discuss how to derive a rate law from a mechanism where the initial step is rate determining, then we will discuss how to derive a rate law from a mechanism where the initial step is not rate determining.

Mechanism where the Initial Step is Rate Determining

Let's revisit the decomposition of ozone:

$$\begin{aligned} &\text{step 1:} && \mathrm{O_3}(g) && \xrightarrow{h\nu} && \mathrm{O_2}(g) + \mathrm{O}(g) && \text{slow} \\ &\text{step 2:} && \mathrm{O}(g) + \mathrm{O_3}(g) && \longrightarrow && 2\ \mathrm{O_2}(g) \\ &\text{overall:} && 2\ \mathrm{O_3}(g) && \longrightarrow && 3\ \mathrm{O_2}(g) \end{aligned}$$

Since Step 1 is the slow step, it determines the overall reaction rate. The slow step produces O atoms, which are rapidly consumed in the faster second step. Because the reaction cannot proceed faster than its slowest step, the rate law for the overall reaction is the same as the rate law for Step 1:

$$\text{rate} = k[O_3]$$

The reaction energy diagram in Figure $6.7.1$ illustrates the relative activation energies of the two steps, showing that Step 1, the rate-determining step, has a larger activation energy than Step 2, $E_{a1} > E_{a2}$.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for the first step.

Example $6.7.1$

Consider the following mechanism:

$$\begin{aligned} &\mathrm{NO_2}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{NO_3}(g) + \mathrm{NO}(g)\ (\text{slow}) \\ &\mathrm{NO_3}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{CO_2}(g)\ (\text{fast}) \end{aligned}$$

a) What is the overall reaction?

b) List any reaction intermediates.

c) At temperatures below 225 °C, measurements show that the reaction is second order with respect to $\mathrm{NO_2}$. Is the mechanism consistent with this experimental observation?

Solution

a)

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g)$$

b) $\mathrm{NO_3}$ is an intermediate. It is made in Step 1 and consumed in Step 2.

c) Step 1 is the rate-determining step, so the rate law for that step is the rate law for the overall reaction:

rate = k[NO_2]^2. This is consistent with the rate law determined experimentally.

Mechanism where the Initial Step is not Rate Determining

The rate law for the overall reaction is always governed by the rate determining step, or slow step, of the mechanism. When it's not the first step, the rate law for the slow step will include at least one reaction intermediate. Reaction intermediates cannot be included in a rate law because they are transient species whose concentration depends on the concentration of the initial reactants and the rate of subsequent steps. For this reason, rate laws are always expressed in terms of the concentration of the reactants and products in the overall reaction.

To describe the rate law of the rate determining step in terms of only reactant and product concentrations, we often use the equilibrium assumption which assumes that the preceding fast steps of the mechanism are reversible and quickly reach equilibrium. At equilibrium, the rate of product formation equals the rate of its conversion back to reactants, allowing us to express the concentration of any intermediates in terms of the concentration of the reactant and products.

Consider the following multi-step reaction as an example:

$$2\,\mathrm{NO\,(g)} + \mathrm{Cl_2\,(g)} \longrightarrow 2\,\mathrm{NOCl\,(g)}$$

The currently accepted mechanism for this reaction is:

$$\begin{aligned}
&\text{Step 1:} && \mathrm{NO}(g) + \mathrm{Cl_2}(g) && \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} && \mathrm{NOCl_2}(g) && \text{fast}\\
&\text{Step 2:} && \mathrm{NOCl_2}(g) + \mathrm{NO}(g) && \xrightarrow{k_2} && 2\mathrm{NOCl}(g) && \text{slow}\\
&\text{Overall:} && 2\mathrm{NO}(g) + \mathrm{Cl_2}(g) && \longrightarrow && 2\mathrm{NOCl}(g) &&
\end{aligned}$$

As seen in Figure 6.7.3, the activation energy for the second step is greater than that of the first step, making it the rate-determining step.

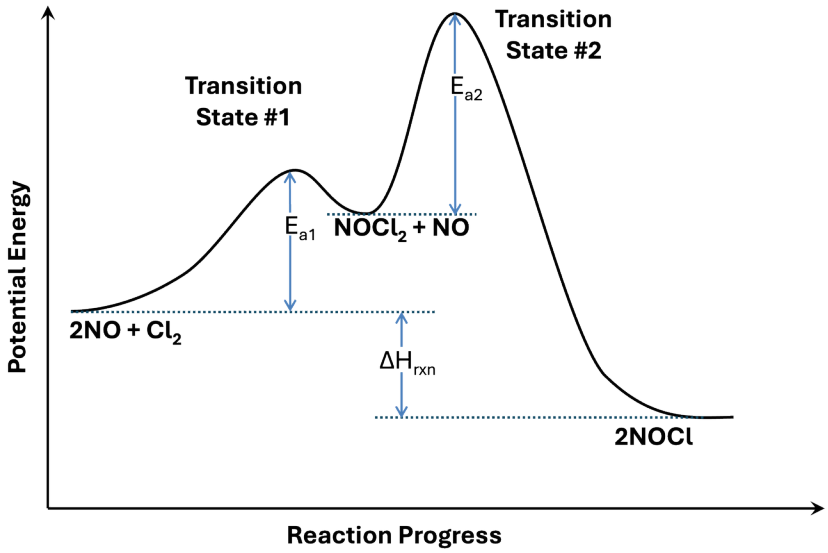


Figure 6.7.3: Reaction energy diagram for the $2\,\mathrm{NO\,(g)} + \mathrm{Cl_2\,(g)} \longrightarrow 2\,\mathrm{NOCl\,(g)}$ reaction

Since Step 2 is slowest step, its rate law determines the overall reaction rate:

$$\text{rate}_2 = k_2\,[\mathrm{NOCl_2}]\,[\mathrm{NO}],$$

However, this expression contains $[NOCl_2]$, the concentration of an intermediate, which is not possible to properly define, and so $[NOCl_2]$ needs to be expressed in terms of concentrations of reactants and/or products.

To do this we need to turn to Step 1, which we assume is a fast and reversible reaction, meaning NO and Cl_2 quickly form $NOCl_2$, and $NOCl_2$ just as quickly breaks down back into NO and Cl_2. Because Step 2 is slower than Step 1, most $NOCl_2$ molecules decompose back into reactants rather than proceeding to Step 2. This allows us to assume that Step 1 is at equilibrium.

At equilibrium, the forward and reverse reaction rates of Step 1 are equal:

$$\text{rate}_1 = \text{rate}_{-1}$$

Since Step 1 has a forward rate constant k_1 and a reverse rate constant k_{-1}, we can express these rates as:

$$k_1[NO][Cl_2] = k_{-1}[NOCl_2]$$

Rearranging for $[NOCl_2]$:

$$[NOCl_2] = \left(\frac{k_1}{k_{-1}}\right)[NO][Cl_2]$$

Substituting this into the rate law for Step 2:

$$\text{rate}_2 = k_2[NOCl_2][NO] = k_2\left(\frac{k_1}{k_{-1}}\right)[NO][Cl_2][NO] = \left(\frac{k_1k_2}{k_{-1}}\right)[NO]^2[Cl_2]$$

Defining a new overall rate constant:

$$k = \frac{k_1k_2}{k_{-1}}$$

we obtain the final rate law:

$$\text{rate} = k\,[NO]^2[Cl_2]$$

This rate law can now be directly compared to experimental data to determine whether the proposed mechanism is consistent with observed reaction kinetics.

Example 6.7.2: Deriving the Overall Rate Law Expression for a Multistep Reaction

Consider the following mechanism:

$$\text{Step 1}: \quad NO(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3(g) \quad \text{fast}$$

$$\text{Step 2}: \quad NO_3(g) + NO(g) \xrightarrow{k_2} 2NO_2(g) \quad \text{slow}$$

a) What is the overall reaction?

b) List any intermediates.

c) Determine the overall rate law.

Solution

a) For the overall reaction, sum the two steps, cancel intermediates, and combine like formulas:

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

b) NO_3 is the intermediate.

c) Write the rate law for the slow step:

rate = $k_2[NO_3][NO]$

Since NO_3 is an intermediate, we need to replace it in the rate law.

Using the fast equilibrium from step 1:

$rate_1 = rate_{-1}$

$k_1[NO][O_2]=k_{-1}[NO_3]$

$$[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$$

Now substitute this expression for $[NO_3]$ into the overall rate law expression:

$$\text{rate} = \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2]$$

Example 6.7.3 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

step 1	$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$	(fast)
step 2	$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$	(slow)
step 3	$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$	(fast)

Write the balanced chemical equation for the overall reaction, identify any intermediates, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction, $\text{rate} = k[NO]^2[H_2]$?

Answer

The overall reaction is $2\,NO\,(g) + 2\,H_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O\,(g)$

The intermediates are N_2O_2 and N_2O.

Rate Determining Step : #2

From Step #2, $rate = k_2[N_2O_2][H_2]$. Since N_2O_2 is an intermediate, we need to replace it in the rate law.

$k_1[NO]^2 = k{-}1[N_2O_2]$.

$$[N_2O_2] == \frac{k_1}{k_{-1}}[NO]^2$$

Substituting into the rate law for step 2 gives:

$rate = \frac{k_1 k_2}{k_{-1}}[NO]^2[H_2]$ which matches the experimentally derived rate law.

Summary

A reaction mechanism is the sequence of elementary steps by which reactants are converted to products. Each elementary step has its own transition state, shown as a maximum on a reaction energy diagram.

Elementary reactions depict actual molecular events and the stoichiometry of an elementary reaction can be used to define reaction orders in a theoetical rate law.

Reaction intermediates are species formed in one step and consumed in a later step. They have fully formed bonds but are typically unstable.

A valid mechanism must (1) sum to the overall balanced equation, (2) consist of plausible (generally unimolecular or bimolecular) steps, and (3) have a rate law consistent with experimental measurements.

The rate-determining step is the slowest step in the mechanism and controls the overall reaction rate. When a fast step precedes the rate-determining step, we often use the equilibrium approximation to eliminate intermediates from the overall rate law.

Understanding the step-by-step mechanism and identifying the rate-determining step allows chemists to explain *why* a reaction follows a particular rate law and predict how changes in conditions will affect the reaction rate.

Glossary

bimolecular elementary reaction
: A reaction that involves the collision of two reactant particles.

elementary reaction
: A step in a reaction mechanism that explicitly shows which particles collide, break apart, or rearrange to form the products and/or intermediates.

rate determining step
: The slowest step in the reaction mechanism; determines the overall reaction rate.

reaction intermediate
: A species with fully formed bonds that appears as a product in one step but is consumed in a subsequent step.

reaction mechanism
: Step-by-step series of simpler reactions by which an overall reaction takes place.

termolecular elementary reaction
: A rare reaction that involves three reactant particles colliding simultaneously.

transition state
: A high-energy intermediate in which bonds are partially broken and formed.

unimolecular elementary reaction
: A reaction that involves the rearrangement or decomposition of a single reactant molecule.

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6.8: Catalysis

Learning Objectives

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams

Many chemical processes benefit from faster reaction rates. One way to speed up reactions is by increasing the temperature, but high temperatures can cause problems: heat-sensitive compounds may break down, unwanted byproducts can form, and heating can be expensive. Another way to increase the reaction rate is to add a catalyst, a substance that increases the rate of reaction without being consumed itself.

How does a catalyst work?

A catalyst increases the rate of reaction by altering the mechanism, allowing the reaction to proceed via a pathway with lower activation energy than the uncatalyzed reaction.

This lower activation energy results in an increase in rate as described by the Arrhenius equation. Because the catalyst lowers the activation energy for both the forward and reverse reactions, it speeds up both directions. Adding a catalyst does not change the equilibrium constant or shift the equilibrium position; the system reaches equilibrium faster (see the later chapter on chemical equilibrium). A catalyzed mechanism generally involves at least two steps: one where the catalyst interacts with a reactant to form an intermediate substance, and one where the intermediate decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form the product. In this way, the catalyst is involved in the reaction mechanism but is not consumed by the reaction.

Consider a simple one-step bimolecular reaction: $X + Y \rightarrow Z$ and its energy diagram in Figure $6.8.1$

In the catalyzed reaction, the same overall reaction proceeds via two steps:

- Step 1: $X + \text{catalyst} \rightarrow \text{Intermediate}$
- Step 2: $\text{Intermediate} + Y \rightarrow Z + \text{catalyst}$

Key points:

- The lower activation energy of the catalyzed pathway increases reaction rates.
- The catalyst is used and then regenerated, so it does not appear in the overall net reaction.
- A catalyst is different from an intermediate:

  A catalyst is consumed as a reactant in one step and produced as a product in another.

  An intermediate is first produced as a product in one step and then consumed as a reactant in another.

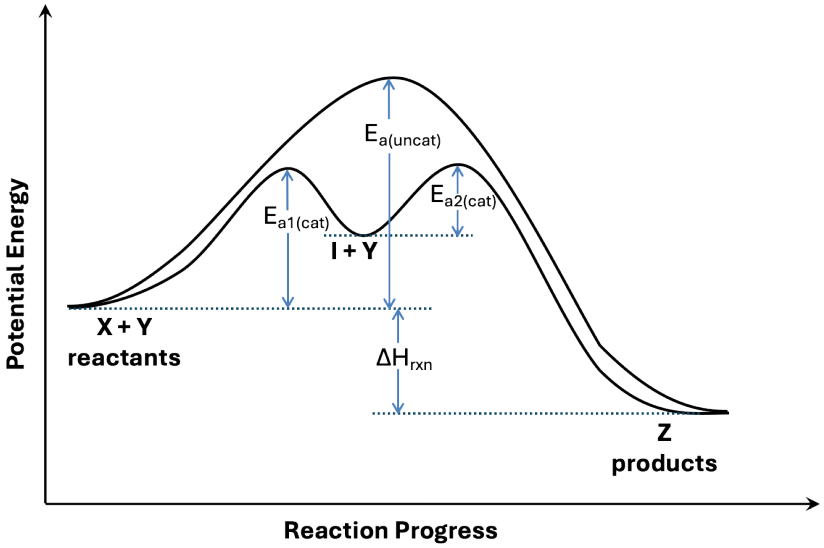


Figure 6.8.1: Reaction energy diagram for the uncatalyzed reaction of X + Y ⟡ Z (single step with higher activation energy) and the catalyzed reaction (two steps, lower activation energy). A catalyst increases reaction rate by providing a new reaction pathway with a lower activation energy. The overall reaction remains the same.

An important example of catalysis is the destruction of ozone (O_3) in Earth's stratosphere (10–40 km above the surface). Stratospheric ozone is crucial because it absorbs ultraviolet (UV) radiation from the sun, preventing harmful UV rays from reaching Earth's surface, where they can damage living organisms, including humans.

Ozone breaks down when it absorbs UV radiation, following this reaction mechanism:

$$\begin{aligned} \text{Step 1: (fast)} \quad & O_3(g) \xrightarrow{h\nu} O_2(g) + O(g) \\ \text{Step 2: (slow)} \quad & O_3(g) + O(g) \longrightarrow 2\ O_2(g) \\ \text{Overall:} \quad & 2\ O_3(g) \xrightarrow{h\nu} 3\ O_2(g) \end{aligned}$$

Certain substances, such as chlorofluorocarbons (CFCs)—once used in air conditioners and aerosol sprays—release chlorine (Cl) atoms in the stratosphere when exposed to UV light. These Cl atoms act as catalysts, accelerating ozone destruction. For example, the CFC CF_2Cl_2 (dichlorodifluoromethane) absorbs UV light, breaking a $C{-}Cl$ bond and releasing a Cl atom. This chlorine atom then catalyzes ozone breakdown through the following simplified mechanism:

$$\begin{aligned} \text{Step 1: (slow)} \quad & Cl(g) + O_3(g) \longrightarrow O_2(g) + ClO(g) \\ \text{Step 2: (fast)} \quad & O_3(g) + ClO(g) \longrightarrow 2\ O_2(g) + Cl(g) \\ \text{Overall:} \quad & 2\ O_3(g) \longrightarrow 3\ O_2(g) \end{aligned}$$

- In Step 1, a chlorine atom (Cl) reacts with ozone, forming oxygen (O_2) and chlorine monoxide (ClO).
- In Step 2, ClO reacts with another ozone molecule, forming two O_2 molecules and regenerating the Cl atom.
- Since Cl is consumed and then re-formed it is a catalyst. Conversely, ClO is produced and consumed and so it is a reaction intermediate.

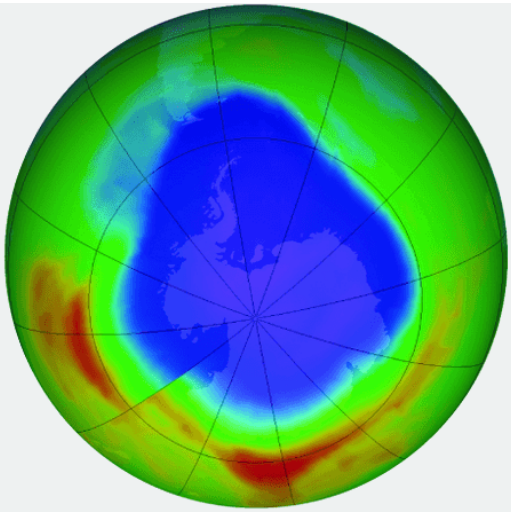
A single chlorine atom can destroy up to 100,000 ozone molecules before it reacts with another substance and is removed from the stratosphere. This leads to ozone depletion, reducing Earth's protection from UV radiation and increasing risks like skin cancer, cataracts, and environmental damage.

Mario J. Molina

In 1995, the Nobel Prize in Chemistry was awarded to Paul J. Crutzen, Mario J. Molina, and F. Sherwood Rowland for their groundbreaking work in atmospheric chemistry, specifically their research on the formation and decomposition of ozone.



(a)



(b)

Figure 6.8.2: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

Mario Molina (born 1943), a Mexican chemist, conducted much of his research at the Massachusetts Institute of Technology (MIT). In 1974, he and F. Sherwood Rowland published a landmark paper in the journal Nature, one of the leading peer-reviewed scientific journals. Their research revealed that chlorofluorocarbons (CFCs)—gases commonly used in refrigeration and aerosol sprays—posed a serious threat to the ozone layer in Earth's upper atmosphere.

The ozone layer plays a critical role in protecting life on Earth by absorbing harmful ultraviolet (UV) radiation from the Sun. Molina and Rowland's research demonstrated that chemical reactions involving CFCs could deplete ozone, leading to the formation of the Antarctic ozone hole. As the ozone layer thins, more UV radiation reaches Earth's surface, increasing the risk of skin cancer, cataracts, and environmental damage.

Their work led to the adoption of the Montreal Protocol in 1987, an international treaty that phased out the production of ozone-depleting chemicals. Today, the treaty has 197 signatory countries, making it one of the most successful environmental agreements in history. The ozone layer is now recovering, demonstrating the global impact of their research.

Homogeneous Catalysts

A homogeneous catalyst is in the same phase (solid, liquid, or gas) as the reactants. It interacts with a reactant to form an intermediate, which then breaks down or reacts with another substance to regenerate the original catalyst and form the final product.

For example, chlorine atoms (Cl) act as homogeneous catalysts in ozone decomposition because all reactants are in the gas phase.

Heterogeneous Catalysts

A heterogeneous catalyst is in a different phase than the reactants. These catalysts are often solid materials with large surface areas, where the reaction takes place. They speed up reactions by providing a surface where reactant molecules can interact and react more efficiently than they would in the gas or solution phase alone.

One well-known heterogeneous catalyst is nickel (Ni), which is used to hydrogenate carbon–carbon double bonds in polyunsaturated fats and oils. This reaction converts unsaturated fats (containing double bonds) into saturated fats (containing only single bonds). An example of this process is the hydrogenation of ethylene, as shown in Figure 6.8.3.

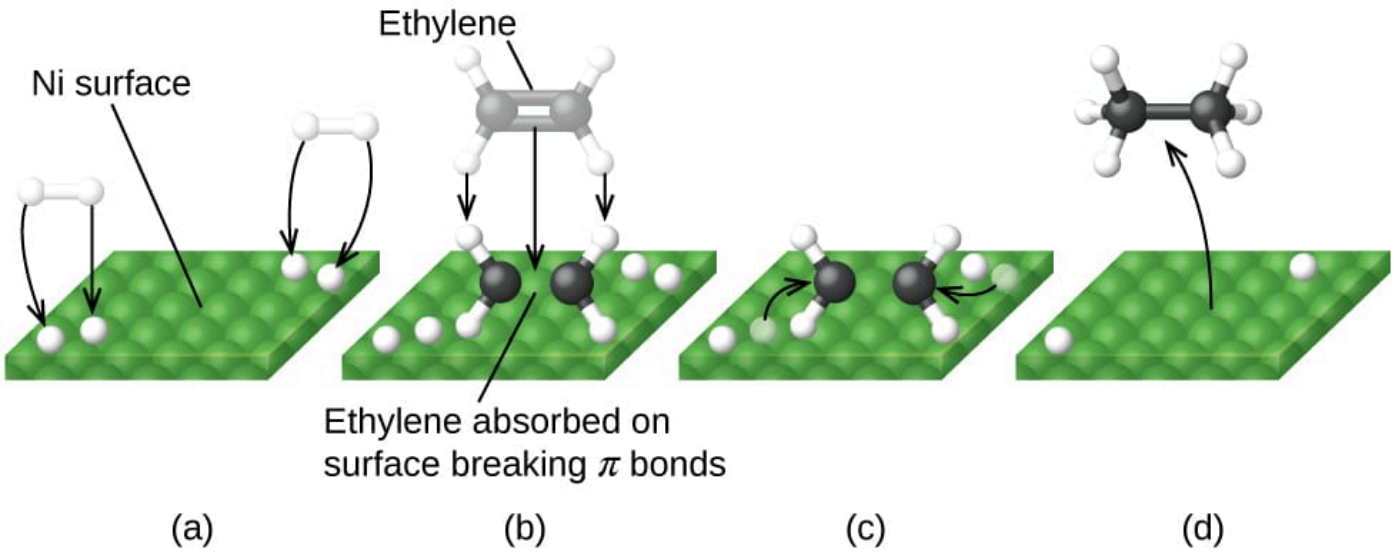


Figure 6.8.3: There are four steps in the Ni catalysis of the reaction $\mathrm{C_2H_4 + H_2 \longrightarrow C_2H_6}$:

a) Adsorption of Hydrogen: Hydrogen gas ($\mathrm{H_2}$) binds to the nickel surface, breaking the $\mathrm{H{-}H}$ bonds and forming $\mathrm{Ni{-}H}$ bonds.

b) Adsorption of Ethylene: Ethylene ($\mathrm{C_2H_4}$) also binds to the nickel surface, weakening the $\mathrm{C{=}C}$ double bond and forming $\mathrm{Ni{-}C}$ bonds.

c) Surface Diffusion & Reaction: Hydrogen atoms migrate across the surface and react with ethylene, forming new $\mathrm{C{-}H}$ bonds.

d) Desorption: The final product, ethane ($\mathrm{C_2H_6}$), is released because it is not strongly attracted to the nickel surface.

Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol, $\mathrm{CH_3OH}$. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 6.8.4).

Automobile Catalytic Converters

Catalytic converters reduce toxic emissions from gasoline engines by using platinum-rhodium catalysts to speed up reactions that make exhaust gases less harmful.

Modern three-way catalytic converters help convert pollutants into safer substances:

$$\mathrm{2\,NO_2}(g) \longrightarrow \mathrm{N_2}(g) + \mathrm{2\,O_2}(g)$$
$$\mathrm{2\,CO}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2\,CO_2}(g)$$
$$\mathrm{2_8\,CH_{18}}(g) + \mathrm{25\,O_2}(g) \longrightarrow \mathrm{16\,CO_2}(g) + \mathrm{18\,H_2O}(g)$$

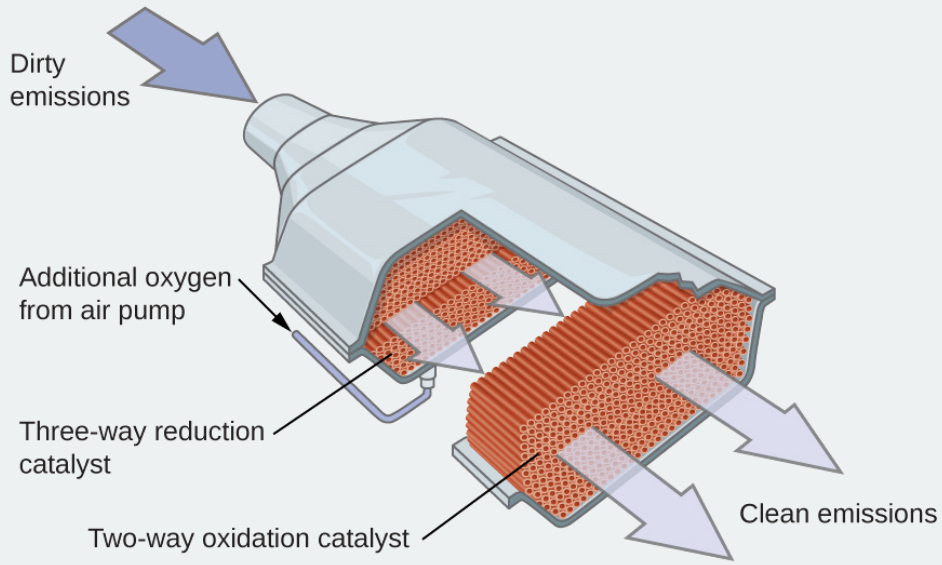


Figure 6.8.4: A catalytic converter allows for more complete combustion of carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Figure 6.8.4 shows how a catalytic converter functions. As exhaust gases enter, an air pump adds extra oxygen to promote complete combustion. The metal catalyst provides a surface where the reactions take place, converting toxic emissions into cleaner gases. The final exhaust contains mostly nitrogen, carbon dioxide, and water vapor, significantly reducing pollution. To work efficiently, catalytic converters must reach high temperatures. Many modern systems use electric preheaters to activate the catalyst faster, ensuring effective emissions reduction even before the engine warms up.

By converting harmful gases into safer ones, catalytic converters help reduce air pollution and protect human health.

Enzymes: Biological Catalysts

Millions of chemical reactions occur within our cells every minute, but without catalysts, most would be too slow to sustain life. Biological catalysts, known as enzymes, dramatically increase reaction rates, often by factors of 10^6 to 10^{20}.

For example, the breakdown of carbonic acid (H_2CO_3) in the lungs:

$$H_2CO_3\,(aq) \longrightarrow CO_2\,(g) + H_2O\,(l)$$

occurs at only ~10^{-7} M/s at room temperature—far too slow to meet the body's needs. The enzyme carbonic anhydrase speeds up this reaction by over a million times, ensuring rapid CO_2 production and removal.

Like all catalysts, enzymes lower activation energy by forming a lower-energy transition state. The reactant(s) in an enzyme-catalyzed reaction are called substrates. Enzymes interact with substrates through hydrogen bonds, ionic attractions, or dipole-dipole interactions. Many enzymes recognize only one specific substrate or a closely related group of molecules. Even a small structural change (such as adding a single methyl group, $-CH_3$) can prevent binding.

Enzymes are usually large protein molecules, but only a small region, the active site, binds the substrate and carries out the reaction. The unique shape of the active site allows enzymes to recognize and act on specific molecules, ensuring precise control over biochemical reactions.

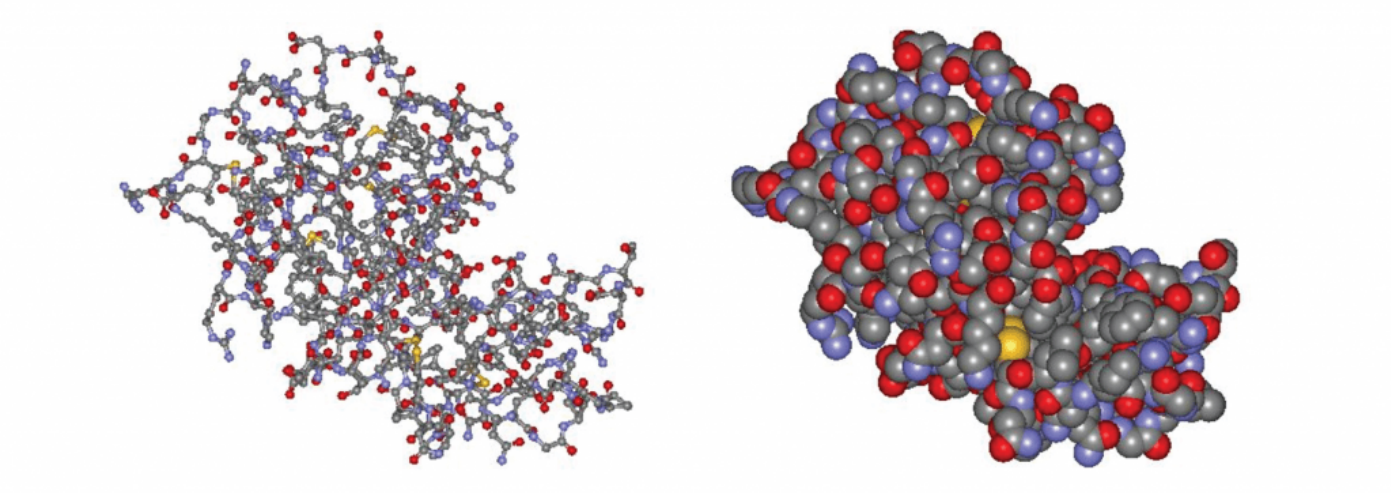


Figure 6.8.5 *Structure of the enzyme lysozyme. Left: ball-and-stick model. Right: space filling model. The cleft in the middle right is the active site, where substrate molecules fit. (Structures from http://lysozyme.co.uk.)*

Models of Enzyme Function

In 1890, Emil Fischer proposed the lock-and-key model, where the substrate fits precisely into the enzyme's active site, like a key fitting into a lock.

In 1958, Daniel E. Koshland Jr. refined this idea with the induced-fit model. He suggested that the enzyme and substrate adjust their shapes upon binding, improving the fit. This explains both enzyme specificity and how enzymes speed up reactions.

- As the substrate interacts with the enzyme, it distorts (atoms shift, bonds stretch, and reactive groups move closer together) to a structure closer to the transition state. This rearrangement lowers the activation energy, accelerating the reaction.
- Only molecules with the correct shape and functional groups can properly bind to the enzyme's active site.

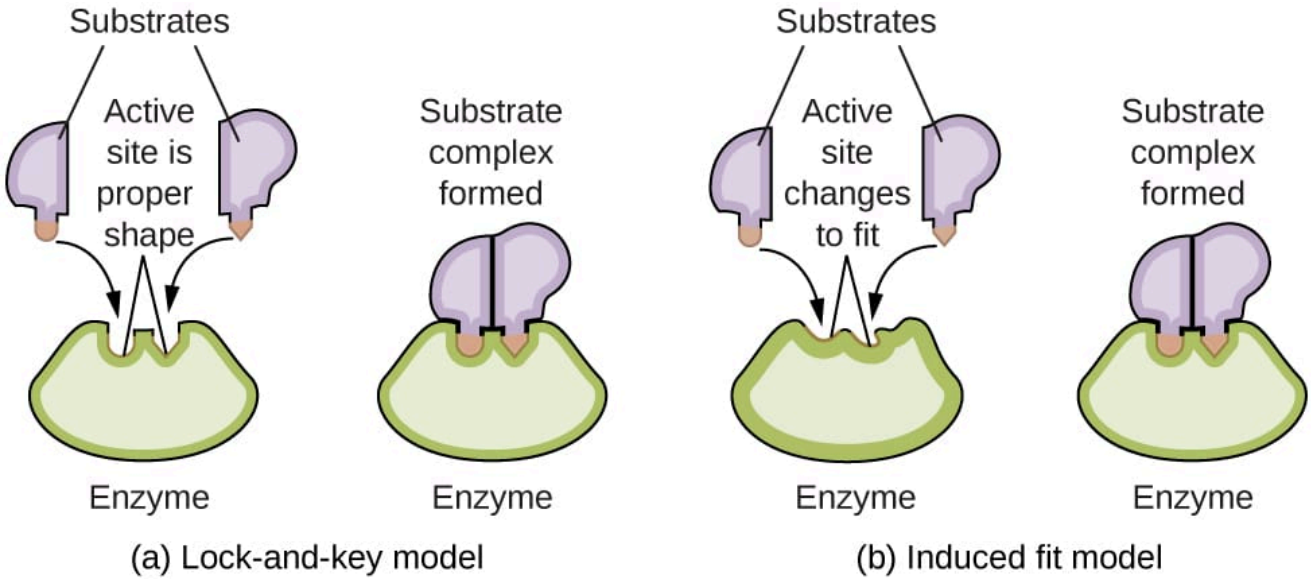


Figure 6.8.6: (a) in the lock-and-key model, the enzyme's active site has a fixed shape that matches the substrate exactly. (b) In the induced-fit model, the active site is somewhat flexible, adjusting its shape to accommodate the substrate.

Enzyme Kinetics: Michaelis-Menten Mechanism

The Michaelis-Menten mechanism describes how enzymes catalyze reactions through a two-step process. An enzyme (E) first binds with a substrate (S) to form an enzyme-substrate complex (ES), which then breaks down to release the product (P) while regenerating the enzyme. The overall reaction is:

$$\text{S} \rightarrow \text{P}$$

with the simple two-step mechanism:

$$\text{step 1: (fast)} \qquad E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$\text{step 2: (slow)} \qquad ES \xrightarrow{k_2} P + E$$

The second step is rate determining.

Enzyme kinetics studies are typically carried out by measuring the reaction rate as a function of the concentration of substrate and the concentration of enzyme. The rate of the catalyzed reaction can be measured by observing the rate of the production of the product:

$$rate = \frac{\Delta[P]}{\Delta t}$$

Initially, as the substrate concentration increases, the reaction rate also increases because more enzyme-substrate complexes (ES) are formed. In this region, the reaction follows first-order kinetics, meaning the rate is proportional to [S]:

rate = k[S].

However, once all enzyme active sites are occupied, adding more substrate does not increase the rate. At this point, the reaction reaches a maximum rate and becomes zero-order in [S], meaning the rate is independent of substrate concentration (Figure 6.8.7).

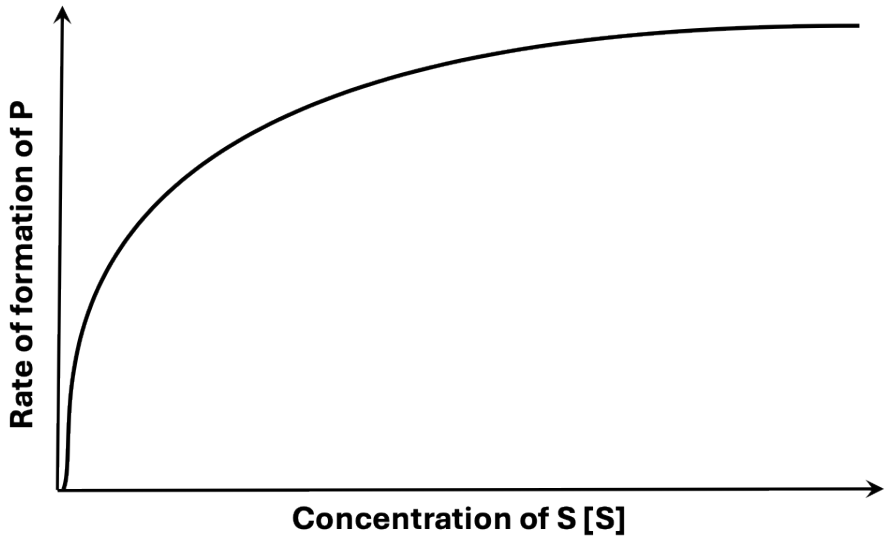


Figure 6.8.7: Plot of rate of formation of Product (P) versus the substrate concentration, [S], in an enzyme-catalyzed reaction.

Chemistry in Everyday Life: Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes play a crucial role in metabolism, and a deficiency in certain enzymes can lead to serious health conditions. Glucose-6-phosphate dehydrogenase (G6PD) deficiency is the most common enzyme deficiency in humans. This enzyme, shown in Figure 6.8.8, is essential for producing NADPH, a molecule that protects red blood cells from oxidative damage.

When G6PD is deficient, red blood cells lose their ability to maintain glutathione, an antioxidant that prevents damage to proteins like hemoglobin. Without enough glutathione, hemoglobin breaks down, leading to jaundice and other complications.

People with G6PD deficiency must avoid certain foods and medications that can trigger red blood cell damage.

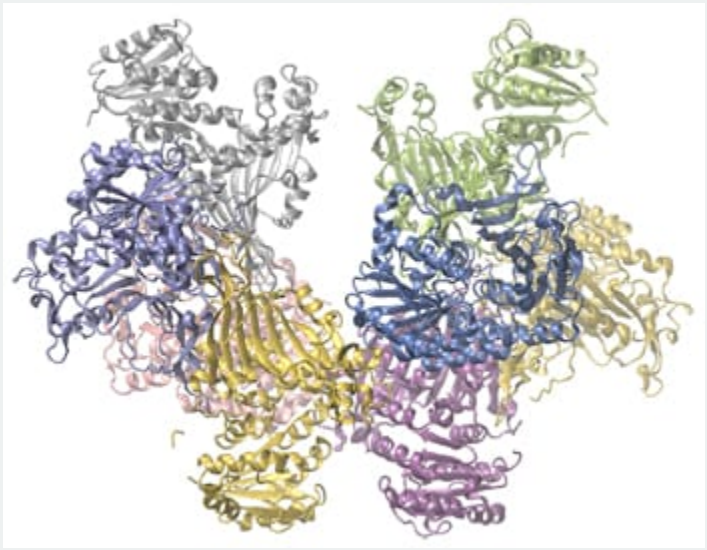


Figure 6.8.8: Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.Summary

Summary

Catalysts speed up reactions by providing a lower-energy pathway, but they are not consumed in the reaction.

In heterogeneous catalysis, catalysts provide a solid surface where reactants bind (adsorption).

In homogeneous catalysis, catalysts and reactants exist in the same phase.

Enzymes are biological catalysts that dramatically increase reaction rates and are highly specific to their substrates.

In enzyme-catalyzed reactions, the substrate binds to the enzyme's active site, forming a temporary enzyme-substrate complex before converting into the product.

Glossary

enzyme
: A biological catalyst; usually large protein molecules with a small active site that binds the substrate and carries out the reaction.

heterogeneous catalyst
: A catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur.

homogeneous catalyst
: A catalyst present in the same phase as the reactants.

induced-fit model
Model of enzyme function where the enzyme and substrate adjust their shapes upon bindng to improve the fit.

lock-and-key model
Model of enzyme function where the substrate fits precisely into the enzyme's active site.

Michaelis-Menten mechanism
Describes how enzymes catalyze reactions through a two-step process; an enzyme binds a substrate to form an enzyme-substrate complex, which then breaks down to release the product while regenerating the enzyme.

substrate
A reactant in an enzyme-catalyzed reaction.

Footnotes

1. "The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, Nobel Prizes Chemistry [www.nobelprize.org].

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6.E: Chemical Kinetics (Exercises)

Reaction Rates

Exercise $6.E.1$*

What is the difference between average rate, initial rate, and instantaneous rate?

Answer available at the end of this section.

Exercise $6.E.2$*

Ozone decomposes to oxygen according to the equation $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of O_2.

Answer available at the end of this section.

Exercise $6.E.3$*

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3\,F_2(g) \longrightarrow 2\,ClF_3(g)$. When $[Cl_2]$ is decreasing at 0.10 M/s, how fast is $[ClF_3]$ increasing?

Answer available at the end of this section.

Exercise $6.E.4$*

Consider the following reaction in aqueous solution:

$$5\,Br^-(aq) + BrO_3{}^-(aq) + 6\,H^+(aq) \longrightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is 3.5×10^{-4} $M\ s^{-1}$, what is the rate of appearance of $Br_2(aq)$ at that moment?

Answer available at the end of this section.

Exercise $6.E.5$**

Write a balanced equation for the reaction with this rate expression:

$$rate = -\frac{\Delta[SO_2]}{\Delta t} = -\frac{\Delta[CO]}{3\Delta t} = \frac{\Delta[CO_2]}{2\Delta t} = \frac{\Delta[COS]}{\Delta t}$$

Answer available at the end of this section.

Exercise $6.E.6$**

A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.952	0.625	0.465	0.370	0.308	0.230

a. Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
b. Use the rate found in part (a) to determine the average rate of formation of *B* between 0.00 s and 10.0 s.

Answer available at the end of this section.

Rate Law

Exercise $6.E.7$*

What is the order with respect to the following reactants?

a. Doubling the concentration of a reactant increases the rate of a reaction four times.
b. Tripling the concentration of a different reactant increases the rate of a reaction three times.

Answer available at the end of this section.

Exercise $6.E.8$*

How much and in what direction will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[{\mathrm{NO_2}}^2]$?

a. Decreasing the pressure of $\mathrm{NO_2}$ from 0.50 atm to 0.250 atm.
b. Increasing the concentration of CO from 0.01 M to 0.03 M.

Answer available at the end of this section.

Answer available at the end of this section.

Exercise $6.E.9$*

Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to the depletion of the ozone layer. The reaction $\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$ is first order with respect to both NO and $\mathrm{O_3}$ with a rate constant of 2.20 × 10^7 $M^{-1}s^{-1}$. What is the rate of disappearance of NO when [NO] = 3.3 × 10^{-6} M and $[\mathrm{O_3}]$ = 5.9 × 10^{-7} M?

Answer available at the end of this section.

Exercise $6.E.10$*

The rate law for the following reaction

$$\mathrm{BrO_3}^-(aq) + 5\,\mathrm{Br}^-(aq) + 6\,\mathrm{H}^+(aq) \longrightarrow 3\,\mathrm{Br_2}(aq) + 3\,\mathrm{H_2O}(l)$$

is $\text{rate} = [\mathrm{BrO_3}^-][\mathrm{Br}^-][\mathrm{H}^+]^2$.

a. Give the reaction order with respect to each reactant and the overall reaction order.

b. By what factor does the rate change if $[BrO_3^-]$ is doubled?

c. By what factor does the rate changes if $[Br^-]$ is halved?

d. By what factor does the rate change if $[H^+]$ is doubled?

Answer available at the end of this section.

Exercise $6.E.11$**

From the following data, determine the rate equation, the rate constant, and the order with respect to *A* for the reaction $A \longrightarrow 2C$.

[*A*] (M)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (M/h)	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Answer available at the end of this section.

Exercise $6.E.12$**

Nitric oxide reacts with chlorine according to the equation:

$$2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

$[NO]$ **(M)**	$[Cl_2]$ **(M)**	**Rate (M/h)**
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law? What is the rate constant?

Answer available at the end of this section.

Exercise $6.E.13$**

Under certain conditions, the decomposition of ammonia on a metal surface gives the following data:

$[NO]$ **(M)**	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (M/h)	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate law and the rate constant for this reaction.

Answer available at the end of this section.

Exercise 6.E.14**

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

$$H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

Determine the rate equation, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (M)	0.30	0.60	0.60
[NO] (M)	0.35	0.35	0.70
Rate (M/s)	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

Answer available at the end of this section.

Integrated Rate Laws

Exercise 6.E.15*

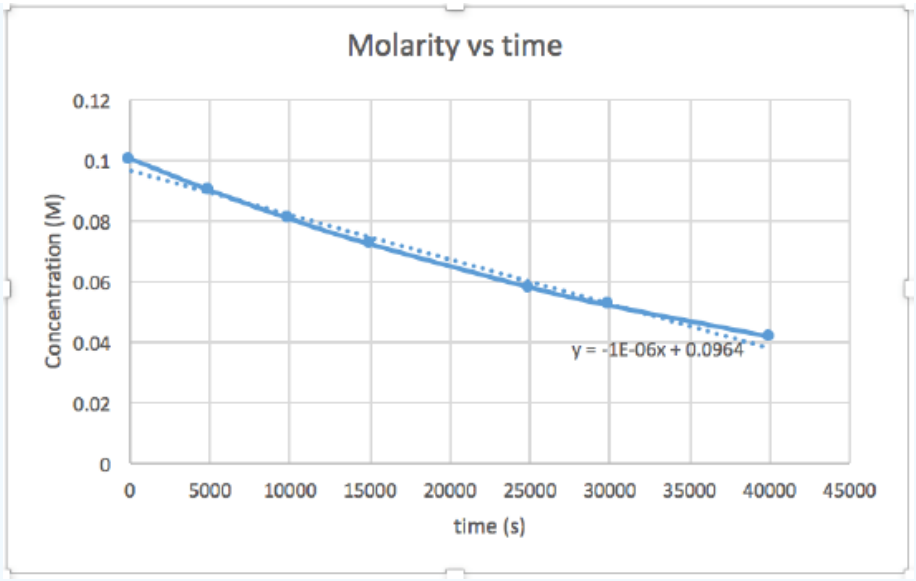
Describe how graphical methods can be used to determine the order of a reaction and its rate constant from measurements of the concentration of *A* with time.

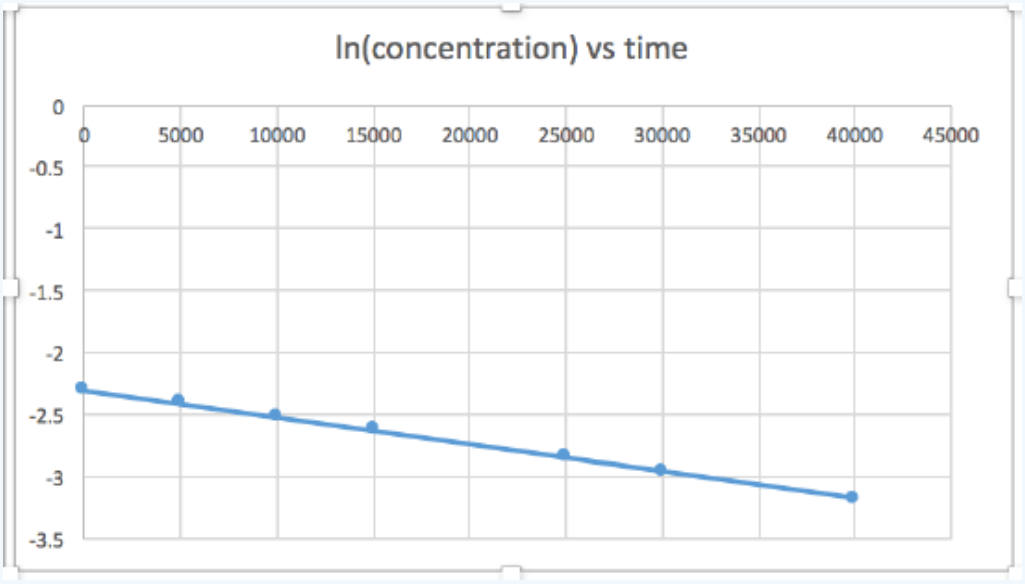
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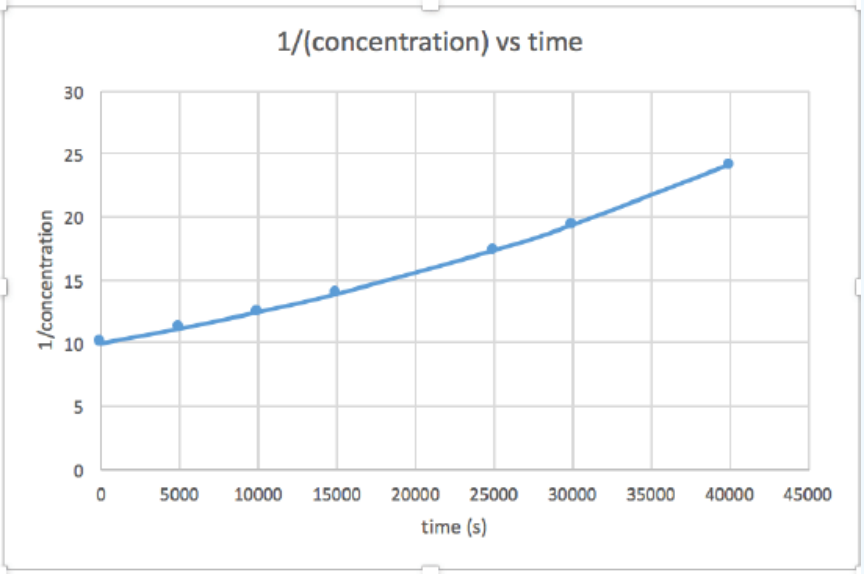
Exercise 6.E.16**

Use the graphs provided to determine the order of the following reaction: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4	2.50×10^4	3.00×10^4	4.00×10^4
[SO2Cl2] (*M*)	0.100	0.0896	0.0802	0.0719	0.0577	0.0517	0.0415


Molarity vs time
Concentration (M)
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
time (s)
y = -1E-06x + 0.0964


ln(concentration) vs time
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0
5000
10000
15000
20000
25000
30000
35000
40000
45000



Answer available at the end of this section.

Exercise $6.E.17$**

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

Answer available at the end of this section.

Exercise $6.E.18$**

In a first-order reaction, 95% of the original amount of reactant decomposes in 122 minutes. What is the half-life of this reaction?

Answer available at the end of this section.

Exercise $6.E.19$**

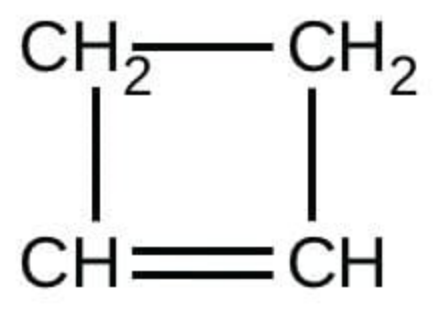
The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*.

The rate constant for the reaction was determined to be 2.42 $M^{-1}s^{-1}$. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Answer available at the end of this section.

Exercise $6.E.20$**

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene $(CH_2{=}CH{-}CH{=}CH_2)$ has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. It is isomeric with cyclobutene:



The isomerization of cyclobutene to butadiene is a first-order reaction, and the rate constant has been measured as 2.0 × 10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 Torr.

Answer available at the end of this section.

Exercise $6.E.21$*

The reaction $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ has the following rate law: $\mathrm{rate} = k[\mathrm{NO_2}^2]$. If the $[\mathrm{NO_2}]$ changes from 1.35 x 10^{-3} M to 1.29 x 10^{-3} M in 10.0 s, what is the rate constant for the reaction?

Answer available at the end of this section.

Collision Theory

Exercise $6.E.22$*

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Answer available at the end of this section.

Exercise $6.E.23$*

How does an increase in temperature affect rate of reaction?

Answer available at the end of this section.

Exercise $6.E.24$**

For a reversible reaction, the enthalpy change of the forward reaction is 37 kJ/mol, and the activation energy of the forward reaction is 96 kJ/mol.

Determine the activation energy of the reverse reaction. Provide a sketch of the potential energy vs. the progress of the reaction.

Answer available at the end of this section.

Exercise 6.E.25**

The rate constant for the decomposition of acetaldehyde (\(\ce{CH3CHO}\)) to methane (\(\ce{CH4}\)) and carbon monoxide (\(\ce{CO}\)) in the gas phase is 1.1 × 10^{-2} M^{-1}s^{-1} at 703 K and 4.95 M^{-1}s^{-1} at 865 K. Determine the activation energy for this decomposition.

Answer available at the end of this section.

Exercise 6.E.26**

An elevated level of the enzyme alkaline phosphatase (ALP) in the serum is an indication of possible liver or bone disorders. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Answer available at the end of this section.

Reaction Mechanisms

Exercise 6.E.27*

Nitrogen(II) oxide, \(\ce{NO}\), reacts with hydrogen, \(\ce{H2}\). Here is a proposed mechanism:

$$2\,\mathrm{NO} + \mathrm{H_2} \longrightarrow \mathrm{N_2} + \mathrm{H_2O_2}\ (\mathrm{slow})$$

$$\mathrm{H_2O_2} + \mathrm{H_2} \longrightarrow 2\,\mathrm{H_2O}\ (\mathrm{fast})$$

a. What is overall reaction?

b. Identify any intermediates.

c. What is the molecularity and rate law for each step?

d. Is the mechanism consistent with the experimentally determined rate law: $\mathrm{rate} = k[\mathrm{NO}][\mathrm{H_2}]$ rate = k[NO][H2]?

Answer available at the end of this section.

Exercise 6.E.28**

The reaction of CO with $\mathrm{Cl_2}$ gives phosgene ($\mathrm{COCl_2}$), a pulmonary agent that was used in World War I. Use the mechanism shown here to complete the following exercises:

$\mathrm{Cl_2}(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,\mathrm{Cl}(g)$ (fast)

$\mathrm{CO}(g) + \mathrm{Cl}(g) \xrightarrow{k_2} \mathrm{COCl}(g)$ (slow)

$\mathrm{COCl}(g) + \mathrm{Cl}(g) \xrightarrow{k_3} \mathrm{COCl_2}(g)$ (fast)

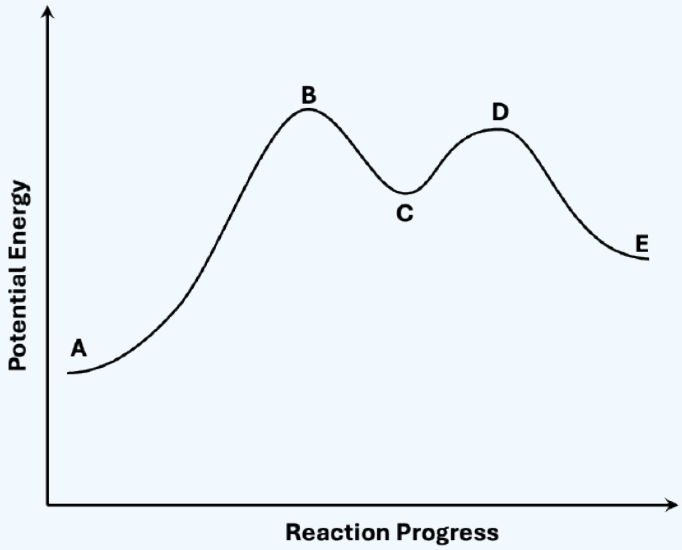
a. Write the overall reaction.
b. Identify all intermediates.

c. Write the rate law for each elementary reaction.
d. Write the overall rate law expression.

Answer available at the end of this section.

Exercise $6.E.29$*

Consider the following reaction energy diagram:



a. How many elementary steps are in the mechanism?

b. Which step is the rate-determining step?

c. What do B and D correspond to?

d. What does C correspond to?

e. Is the overall reaction exothermic or endothermic?

Answer available at the end of this section.

Catalysis

Exercise $6.E.30$*

Consider the following mechanisms.

a.

$$\begin{aligned} \mathrm{O_3} &\xrightarrow{sunlight} \mathrm{O_2 + O} \\ \mathrm{O_3 + Cl} &\longrightarrow \mathrm{O_2 + ClO} \\ \mathrm{ClO + O} &\longrightarrow \mathrm{Cl + O_2} \end{aligned}$$

b.

$$O_3 \xrightarrow{sunlight} O_2 + O$$
$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

For each, give the overall reaction and identify any intermediates and any catalysts.

Answer available at the end of this section.

Additional Problems

Exercise 6.E.31***

Experiments were conducted to study the rate of the reaction represented by this equation.

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol/L)	Initial Concentration, [H2] (mol/L)	Initial Rate of Formation of N2 (M/min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

a. Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
b. Write the overall rate law for the reaction.
c. Calculate the value of the rate constant, *k*, for the reaction. Include units.
d. What is the initial rate when [NO] = 0.0015 M and [H_2]=0.0035M?
e. The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \ \ (fast)$

Step 2: $N_2O_2 + H_2 \xrightarrow{k_2} H_2O + N_2O \ \ (slow)$

Step 3: $N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O \ \ (fast)$

Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

Answer available at the end of this section.

Exercise 6.E.32**

Draw a reaction energy diagram consistent with the mechanism:

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \ \ (fast)$

Step 2: $\mathrm{N_2O_2 + H_2 \xrightarrow{k_2} H_2O + N_2O}\ (slow)$

Step 3: $\mathrm{N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O}\ (fast)$

The overall reaction is exothermic.

Answer available at the end of this section.

Exercise $6.E.33$***

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, $\mathrm{H_2}$, and iodine, $\mathrm{I_2}$. The value of the rate constant, *k*, for the reaction was measured at two different temperatures, and the data are shown here:

Temperature (K)	*k* (M^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
700	?

What is the value of the activation energy (in kJ/mol) for this reaction? What is the rate constant at 700 K?

Answer available at the end of this section.

Exercise $6.E.34$***

Consider the following mechanism:

Step 1: $\mathrm{W + W \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A}\ (fast)$

Step 2: $\mathrm{A + X \xrightarrow{k_2} Y + B}\ (slow)$

Step 3: $\mathrm{B + X \xrightarrow{k_3} Z}\ (fast)$

a. What is the overall reaction?

b. Which step is the rate-determining step?

c. What is the rate law for the reaction?

d. What is the effect on the reaction rate of doubling the [W] and halving the concentration of [X]?

Answer available at the end of this section.

Exercise $6.E.35$**

The following data have been determined for the reaction:

$$\mathrm{I^- + OCl^- \longrightarrow IO^- + Cl^-}$$

	1	2	3
$[\mathrm{I^-}]_{\mathrm{initial}}$ **(M)**	0.10	0.20	0.30

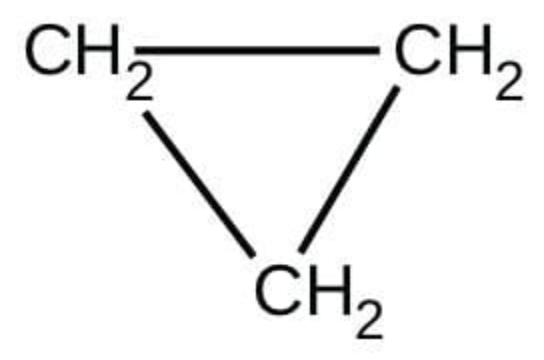
	1	2	3
$[OCl^-]_{initial}$ **(M)**	0.050	0.050	0.010
Rate (M/s)	3.05×10^{-4}	6.10×10^{-4}	1.83×10^{-4}

Determine the rate equation and the rate constant for this reaction.

Answer available at the end of this section.

Exercise 6.E.36**

Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane undergoes a first-order rearrangement with a rate constant of 5.95×10^{-4} s^{-1}. What is the half-life of this reaction in hours? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Answer available at the end of this section.

Exercise 6.E.37**

The overall reaction $H_2 + Br_2 \rightarrow 2\,HBr$ occurs in the following three step mechanism:

i. $Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br$ (forward and reverse reactions are fast)
ii. $Br + H_2 \xrightarrow{k_2} HBr + H$ (slow)
iii. $H + Br_2 \xrightarrow{k_3} HBr + Br$ (fast)

What is the rate law for the entire reaction?

Answer available at the end of this section.

Exercise 6.E.38**

The reaction A + B ⇌ C + D is second-order in A and zero-order in B. The value of the rate constant k is 0.0107 M^{-1} min^{-1}. What is the rate of this reaction when [A] = 0.0010 M and [B] = 0.25 M?

Answer available at the end of this section.

Answers

Exercise $6.E.1$*

The reaction rate is the measure of the change in concentration of the reactants or products per unit time.

Average rate: The change in concentration of a reactant (or product) divided by a specific time interval

Instantaneous rate: The reaction rate at a specific given moment during the reaction.

Initial rate: The instantaneous rate at the start of the reaction (when the product begins to form).

Exercise $6.E.2$*

For the general reaction $aA \rightarrow bB$, the rate can be expressed in terms of the disappearance of (A) or the appearance of (B) as follows:

$$-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = \frac{1}{b}\frac{\Delta[B]}{\Delta t}$$

The rate of a reaction is defined to be positive. Since the concentration of a reactant, [A], decreases, we use a negative sign to ensure the rate remains positive.

The rate must be normalized according to the stoichiometry of the reaction. In the decomposition of ozone to oxygen, two moles of ozone form three moles of oxygen gas. Therefore, the rate of the reaction can be described as:

$$\text{Rate} = -\frac{\Delta[\text{O}_3]}{2\Delta t} = \frac{\Delta[\text{O}_2]}{3\Delta t}$$

Exercise $6.E.3$*

$$rate = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[ClF_3]}{\Delta t}$$

$$\frac{\Delta[ClF_3]}{\Delta t} = 0.20 M/s$$

Exercise $6.E.4$*

Step 1. Define the rate of the reaction.

Recall:

For the general reaction: aA + bB → cC+ dD

$rate = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$

So, for the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l)$

The rate would be: $rate = -\frac{\Delta[Br^-]}{5\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{\Delta[H^+]}{6\Delta t} = \frac{\Delta[Br_2]}{3\Delta t} = \frac{H_2O}{3\Delta t}$

Step 2. Since we are given the rate for the disappearance of Br^-(aq) is $3.5 \times 10^{-4} Ms^{-1}$, and we want to find the rate of appearance of Br_2(aq). Therefore we set the two rates equal to each other.

$rate = -\frac{\Delta[Br^-]}{5\Delta t} = \frac{\Delta[Br_2]}{3\Delta t}$

And,$-\frac{\Delta[Br^-]}{\Delta t} = -3.5 \times 10^{-4} Ms^{-1}$

So, $3.5 \times 10^{-4} Ms^{-1}$ = $\frac{5}{3}\frac{\Delta[Br_2]}{\Delta t}$

Step 3. Now solve the equation.

$\frac{(3.5\times10^{-4} Ms^{-1})(3)}{5} = \frac{\Delta[Br_2]}{\Delta t}$

$\frac{\Delta[Br_2]}{\Delta t} = 2.1 \times 10^{-4} Ms^{-1}$

Exercise $6.E.5$**

For the general reaction: aA + bB → cC+ dD

$rate = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$

Consequently, the sign determines whether the compound is a reactant (negative sign) or a product (positive sign), and the coefficient in the denominator (a, b, c, d) corresponds to the coefficient in the chemical equation.

$$\text{SO}_2 + 3\text{CO} \longrightarrow 2\text{CO}_2 + \text{COS}$$

Exercise $6.E.6$**

a) The change in A from 0s to 10s is 0.625M - 1M = -0.375M

so $\frac{-\triangle A}{\triangle t}$ = 0.375M/10s = 0.0375 M/s

Similarly, the change in A from 10 to 20 seconds is 0.370M - 0.625M = -0.255M

so $\frac{-\triangle A}{\triangle t}$ = 0.255M/(20s - 10s) = 0.0255 M/s

b) Using the equation $\frac{-\triangle A}{2\triangle t} = \frac{\triangle B}{\triangle t}$, we divide the rate in part (a) in half to get 0.0188 M/s from 0 to 10 seconds.

Exercise $6.E.7$*

rate = k[reactant]^{order}

a) Since doubling the concentration increases the rate by a factor of four, the order (the exponent) must be 2. The reaction is second order with respect to the reactant.

b) Since tripling the concentration increases the rate by a factor of three, the order (the exponent) must be 1. The reaction is first order with respect to the reactant.

Exercise $6.E.8$*

Exercise $6.E.8$*

a. Decreasing the pressure by a factor of 2 will reduce the rate by a factor of 4 since the reaction is second order with respect to NO_2.

b. Since CO does not appear in the rate law increasing the concentration will have no effect on the rate.

Exercise $6.E.9$*

rate = k$[\text{NO}][\text{O}_3]$

rate = 2.20 x 10^7 $M^{-1}s^{-1}$ (3.3 × 10^{-6} M)(5.9 × 10^{-7} M) = 4.3 x 10^{-5} M/s

Exercise $6.E.10$*

a. In the rate equation, the orders are given by the exponents of the concentration terms. The overall order is the sum of the individual orders. Therefore, the reaction is:

- First order with respect to $[BrO_3^-]$
- First order with respect to $[Br^-]$
- Second order with respect to $[H^+]$
- Overall reaction order = 1 + 1 + 2 = 4

b. Doubling $[BrO_3^-]$ (which is first order) would increase the rate by a factor of 2.

c. Halving $[Br^-]$ (which is first order) would decrease the rate by a factor of 1/2.

d. Doubling $[H^+]$ (which is second order) would increase the rate by a factor of 2^2 = 4.

Exercise $6.E.11$**

A. Using the experimental data, we can compare the effects of changing [A] on the rate of reaction by relating ratios of [A] to ratios of rates

$$\frac{2.66 \times 10^{-2} M}{1.33 \times 10^{-2} M} = 2$$

and

$$\frac{1.52 \times 10^{-6} M/h}{3.8 \times 10^{-7} M/h} = 4$$

B. From this we know that doubling the concentration of A will result in quadrupling the rate of reaction. The order of this reaction is 2.

C. We can now write the rate equation since we know the order:

$$rate = k[A]^2$$

D. By plugging in one set of experimental data into our rate equation we can solve for the rate constant, k:

$$3.80 \times 10^{-7} M/h = k \times (1.33 \times 10^{-2} M)^2$$

$$k = \frac{3.80 \times 10^{-7} M/h}{1.769 \times 10^{-4} M^2}$$

$$k = 0.00215 M^{-1} h^{-1}$$

Exercise $6.E.12$**

For the general equation,

$aA + bB \rightarrow cC + dD$

The rate can be written as

$rate = k[A]^m[B]^n$ where k is the rate constant, and m and n are the reaction orders.

For our equation

$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

the $rate = k[NO]^m[Cl_2]^n$

Now, we need to find the reaction orders. Reaction orders can only be found through experimental values. We can compare two reactions where one of the reactants has the same concentration for both trials, and solve for the reaction order.

$\frac{rate_1}{rate_2} = \frac{[NO]_1^m[Cl_2]_1^n}{[NO]_2^m[Cl_2]_2^n}$

We can use the data in the table provided. If we plug in the values for rows 1 and 2, we see that the values for the concentration of Cl will cancel, leaving just the rates and the concentrations of NO.

$\frac{1.14 M/h}{4.56 M/h} = \frac{[0.5M]^m}{[1.0M]^m}$

We can now solve for m, and we find that m =2. This means that the reaction order for $[NO]$ is 2.

Now we must find the value of n. To do so, we can use the same equation but with the values from rows 2 and 3. This time, the concentration of NO will cancel out.

$\frac{4.56 M/h}{9.12 M/h} = \frac{[0.5M]^n}{[1.0M]^n}$

When we solve for n, we find that n = 1. This means that the reaction order for $[Cl_2]$ is 1.

We are one step closer to finishing our rate equation.

$rate = k[NO]^2[Cl_2]$

Finally, we can solve for the rate constant. To do this, we can use one of the trials of the experiment, and plug in the values for the rate, and concentrations of reactants, then solve for k.

$1.14 M/h = k[0.5M]^2[0.5M]$

$k = 9.12\ \ M^{-2}h^{-1}$

So, our final rate equation is:

$rate = (9.12\ \ M^{-2}h^{-1})[NO]^2[Cl_2]$

*A common mistake is forgetting units. Make sure to track your units throughout the process of determining your rate constant. Be careful because the units will change relative to the reaction order.

Exercise $6.E.13$**

In the three trials, the rate is the same despite $[NH_3]$ changing. This means that the reaction is zeroth order.

rate = k

k = 1.5 × 10^{-6} M/h

Exercise $6.E.14$**

To find the orders of each reactant, we see that when $[NO]$ doubles but $[H_2]$ doesn't change, the rate quadruples, meaning that the reaction is of second order

with respect to $[NO]$ ($[NO^2]$). When $[H_2]$ doubles but $[NO]$ doesn't change, the rate doubles, meaning that $[H_2]$ is a first order reactant.

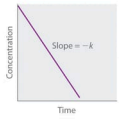
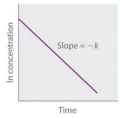
$$\text{rate} = k[NO_2{}^2][H_2]$$

We can use this rate law to determine the value of the rate constant. Plug in the data for reactant concentration and rate from one of the trials to solve for k, the rate constant. In this case, we chose to use the data from trial 1 from the second column of the data table.

$$2.835\text{x}10^{-3}\ \text{M/s} = k[0.30\text{M}]^2[0.35\text{M}]$$

$$k = 0.090\ \text{M}^{-2}\text{s}^{-1}$$

Exercise $6.E.15$*

	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			
Relative rate vs. concentration	[A], *M* / Rate, M/s: 1 / 1; 2 / 1; 3 / 1	[A], *M* / Rate, M/s: 1 / 1; 2 / 2; 3 / 3	[A], *M* / Rate, M/s: 1 / 1; 2 / 4; 3 / 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of *k*, rate constant	M/s	1/s	$M^{-1}s^{-1}$

To determine the order of a reaction when given the data series, one must graph the data as it is, graph it as the natural log of [A], and graph it as 1/[A] versus time. Whatever method yields a straight line will determine the order. Respective of the methods of graphing above, if a straight line is yielded by the first graphing method, it is a 0th order; if by the second method, it's a 1st order; and if by the third graphing method, it's a 2nd order. When the order of the graph is known, a series of equations, given in the above image, can be used with the various points on the graph to determine the value of k. We can see that we need an initial value of A and a final value of A, and both of these would be given by the data.

Zeroth order, when plotting initial concentration versus final concentration, you have a negative linear slope.

$$[A] = [A]_0 - kt$$

First order, when plotting ln[initial concentration] versus ln[final concentration], you have a negative linear slope.

$$\ln[A] = \ln[A]_0 - kt$$

Second order, when plotting the 1/[initial concentration] versus 1/[final concentration], you have a positive linear slope.

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$$

Exercise $6.E.16$**

The plot of $\ln[SO_2Cl_2]$ vs time is linear, so the rate law is $rate = k[SO_2Cl_2]$

Exercise $6.E.17$**

Approach #1

1. Find out how many half-lives to get to 1/64th of initial dose:

$$1 \xrightarrow{t_{1/2}} \frac{1}{2} \xrightarrow{t_{1/2}} \frac{1}{4} \xrightarrow{t_{1/2}} \frac{1}{8} \xrightarrow{t_{1/2}} \frac{1}{16} \xrightarrow{t_{1/2}} \frac{1}{32} \xrightarrow{t_{1/2}} \frac{1}{64}$$

2. Counting the number of half-lives, we see that it takes 6 half-lives to reach 1/64 of the initial concentration. Since the half-life is constant for a first-order reaction, we can multiply 6 x 42 days = 252 days

Approach #2

1. For a first order reaction, the integrated rate law is $ln\frac{[A]_t}{[A]_0} = -kt$

For the half-life, t = $t_{1/2}$ = 42 days and $[A]_t = 0.5[A]_0$ so we can find k.

$$ln\left(\frac{0.5[A]_0}{[A]_0}\right) = -k(42\ days)$$

k = 0.0165 days^{-1}

2. We want the time when the $[A]_t = 1/64[A]_0$.

$$ln\left(\frac{\frac{1}{64}[A]_0}{[A]_0}\right) = -0.0165 days^{-1} t$$

t = 252 days

Exercise $6.E.18$**

To determine the half-life of a first-order reaction, we first calculate the rate constant k using the integrated rate law:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

We're told that 95% of the reactant has decomposed in 122 minutes, so 5% remains:

$$[A]_t = 0.05[A]_0$$

$$\ln\left(\frac{0.05[A]_0}{[A]_0}\right) = -k(122) \quad \Rightarrow \quad \ln(0.05) = -122k$$

$$-2.996 = -122k \quad \Rightarrow \quad k = \frac{2.996}{122} = 0.0246 \text{ min}^{-1}$$

For the half-life, $t = t_{1/2}$ and $[A]_t = 0.5[A]_0$:

$$\ln\left(\frac{0.5[A]_0}{[A]_0}\right) = -(0.0246 \text{ min}^{-1})(t_{1/2})$$

$$t_{1/2} = \frac{0.693}{0.0246} = 28.2 \text{ min}$$

Exercise $6.E.19$**

The second-order integrated rate law is $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

For the half-life, t = $t_{1/2}$ and $[A]_t = 0.5[A]_0$.

$$\frac{1}{0.5(0.500M)} = 2.42M^{-1}s^{-1}t_{1/2} + \frac{1}{(0.500M)}$$

When we plug in the given information, we get:

$$t_{\frac{1}{2}} = \frac{1}{\frac{2.42L}{mol \cdot s}[0.500\frac{mol}{L}]} = 0.826s$$

Notice that the units cancel out to seconds.

Exercise $6.E.20$**

For a first-order gas-phase reaction, the integrated rate law can be written using partial pressures:

$$\ln\left(\frac{P_t}{P_0}\right) = -kt$$

Given:

- $P_0 = 55 \text{ Torr}$
- $k = 2.0 \times 10^{-4} \text{ s}^{-1}$
- $t = 30.0 \text{ min} = 1800 \text{ s}$

Substitute into the rate law:

$$\ln\left(\frac{P_t}{55 \text{ Torr}}\right) = -0.36 \quad \Rightarrow \quad P_t = 55 \text{ Torr} \cdot e^{-0.36} = 38 \text{ Torr}$$

To find the concentration of cyclobutene, use the ideal gas law:

$$[\text{cyclobutene}] = \frac{n}{V} = \frac{P}{RT} = \frac{38 \text{ Torr} \cdot \frac{1 \text{ atm}}{760 \text{ Torr}}}{(0.08206 \frac{\text{L·atm}}{\text{mol·K}})(423 \text{ K})} = 1.4 \times 10^{-3} \text{ mol/L}$$

Exercise $6.E.21$*

The second order integrated rate law is $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

$$k = \frac{\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right)}{t} = \frac{\left(\frac{1}{1.29 \times 10^{-3}M} - \frac{1}{1.35 \times 10^{-3}M}\right)}{10.0s} = 3.45 \ M^{-1}s^{-1}$$

Exercise $6.E.22$*

The two factors that may prevent a collision from producing a chemical reaction are:

1. **Kinetic energy of the reactants**

In order for chemical reactions to occur, molecules require enough velocity to overcome the minimum activation energy needed to reach the transition state.

2. **The orientation of molecules during the collision**

Two molecules have to collide in the right orientation in order for the reaction to occur.

Exercise $6.E.23$*

Collision theory states that the rates of chemical reactions depend on the fraction of molecules with the correct orientation, fraction of collisions with required energy, and the collision frequency. Because the fraction of collisions with required energy is a function of temperature, as temperature increases, the fraction of collisions with required energy also increases. The kinetic energy of reactants also increases with temperature which means molecules will collide more often increasing collisions frequency. With increased fraction of collisions with required energy and collisions frequency, the rate of chemical reaction increases. We see mathematically, from the Arrhenius equation, that temperature and the rate constant are related.

$$k = Ae^{-\frac{E_a}{RT}}$$

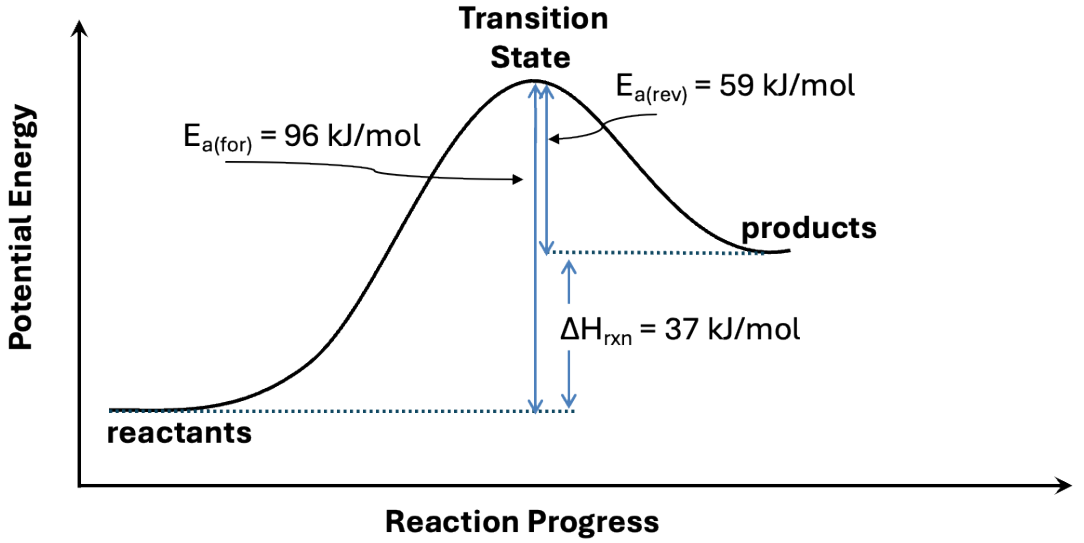
where k is the rate constant, A is the frequency factor, R is 8.3145 $\frac{J}{mol \cdot K}$, E_a is the reaction-specific activation energy in $\frac{J}{mol}$, and T is temperature in K. We see from the equation that k is very sensitive to changes in temperature.

Exercise $6.E.24$**

Because the enthalpy change of the forward reaction is 37 kJ/mol, the products are 37 kJ/mol closer to the transition state than the reactants. The activation

energy for the reverse reaction is $96\,\text{kJ/mol} - 37\,\text{kJ/mol} = 59\,\text{kJ/mol}$.

$\Delta\text{H} = +37\,\text{kJ/mol}$
$\text{E}_\text{a}(\text{forward}) = 96\,\text{kJ/mol}$
$\text{E}_\text{a}(\text{reverse}) = 59\,\text{kJ/mol}$



Exercise $6.E.25$**

When given two rate constants for the same reaction but at two different temperatures, the Arrhenius equation can be rewritten as:

$$ln(\frac{k_2}{k_1}) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

In this problem, all the variables are given except for the E_a (activation energy).

$k_1 = 1.1 \times 10^{-2}\ \frac{L}{mol \cdot s}$
$T_1 = 703\ K$
$k_2 = 4.95\ \frac{L}{mol \cdot s}$
$T_2 = 865\ K$
$R = 8.314\ \frac{J}{mol \cdot K}$ (Ideal Gas Constant)

Now plug in all these values into the equation, and solve for E_a.

$$ln(\frac{4.95\frac{L}{mol \cdot s}}{1.1 \times 10^{-2}\frac{L}{mol \cdot s}}) = \frac{E_a}{8.314\frac{J}{mol \cdot K}}(\frac{1}{703} - \frac{1}{865})$$

$E_a = 1.9 \times 10^5$ J/mol or 190 kJ/mol

Exercise $6.E.26$**

Using the Arrhenius equation:

$$ln(\frac{k_2}{k_1}) = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

Since the rate of reaction increases 1.47 times, $k_2/k_1 = 1.47$. Note that the temperatures must be converted to K.

$$E_a = -\frac{ln\left(\frac{k_2}{k_1}\right)R}{(\frac{1}{T_2} - \frac{1}{T_1})}$$

$$E_a = -\frac{ln\,(1.47)\left(8.314\frac{J}{mol \cdot K}\right)}{(\frac{1}{310K} - \frac{1}{303K})} = 4.30 \times 10^4 J/mol$$

Exercise $6.E.27$*

a. Overall reaction:

Add the two steps and cancel the intermediate (H_2O_2):

$$2\,\text{NO} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}_2$$
$$\text{H}_2\text{O}_2 + \text{H}_2 \longrightarrow 2\,\text{H}_2\text{O}$$

Overall:

$$2\,\text{NO} + 2\,\text{H}_2 \longrightarrow \text{N}_2 + 2\,\text{H}_2\text{O}$$

b. Intermediate: H_2O_2 (formed in Step 1 and consumed in Step 2)

c. Molecularity and rate laws:

- Step 1: Termolecular; *rate* = $k_1[\text{NO}]^2[\text{H}_2]$

- Step 2: Bimolecular; *rate* = $k_2[\mathrm{H_2O_2}][\mathrm{H_2}]$

d. Consistency with experimental rate law:

The rate-determining step of the mechanism suggests a rate law of $k[\mathrm{NO}]^2[\mathrm{H_2}]$, but the experimentally determined rate law is $k[\mathrm{NO}][\mathrm{H_2}]$.

Conclusion: The proposed mechanism is *not consistent* with the experimental rate law.

Exercise $6.E.28$**

a. Overall reaction:

Add all the steps and cancel intermediates:

$$\mathrm{Cl_2} \rightleftharpoons 2\,\mathrm{Cl}$$
$$\mathrm{CO} + \mathrm{Cl} \longrightarrow \mathrm{COCl}$$
$$\mathrm{COCl} + \mathrm{Cl} \longrightarrow \mathrm{COCl_2}$$

Cancelling intermediates ($2\,\mathrm{Cl}$ and COCl):

$$\mathrm{Cl_2} + \mathrm{CO} \longrightarrow \mathrm{COCl_2}$$

b. Intermediates: Cl, COCl

c. Rate law for each step:

- Step 1 (fast equilibrium):
  Forward: $\mathrm{rate_{fwd}} = k_1[\mathrm{Cl_2}]$
  Reverse: $\mathrm{rate_{rev}} = k_{-1}[\mathrm{Cl}]^2$
- Step 2 (slow): $\mathrm{rate} = k_2[\mathrm{CO}][\mathrm{Cl}]$
- Step 3 (fast): $\mathrm{rate} = k_3[\mathrm{COCl}][\mathrm{Cl}]$

d. Overall rate law:

Based on the slow (rate-determining) step:

$$\mathrm{rate} = k_2[\mathrm{CO}][\mathrm{Cl}]$$

Eliminate the intermediate Cl using the equilibrium from Step 1:

$$\mathrm{rate_{for}} = \mathrm{rate_{rev}}$$

$$k_1[\mathrm{Cl_2}] = k_{-1}[\mathrm{Cl}]^2 \Rightarrow [\mathrm{Cl}] = \sqrt{\frac{k_1}{k_{-1}}[\mathrm{Cl_2}]}$$

Substitute into the rate law:

$$\mathrm{rate} = k_2[\mathrm{CO}] \cdot \sqrt{\frac{k_1}{k_{-1}}[\mathrm{Cl_2}]} = k[\mathrm{CO}]\sqrt{[\mathrm{Cl_2}]}$$

Exercise $6.E.29$*

a. There are 2 elementary steps, indicated by the two peaks (activation energy barriers) in the diagram.

b. The first step is the rate-determining step because it has the highest activation energy (the tallest peak).

c. B and D are transition states: high-energy, unstable configurations that occur at the peak of each step.

d. C is a reaction intermediate. It forms in the first step and is consumed in the second, appearing in the valley between the two peaks.

e. The reaction is endothermic because the energy of the products (E) is higher than the energy of the reactants (A), indicating that energy is absorbed overall.

Exercise $6.E.30$*

a.

$$\mathrm{O_3} \xrightarrow{sunlight} \mathrm{O_2} + \cancel{\mathrm{O}}$$
$$\mathrm{O_3} + \cancel{\mathrm{Cl}} \longrightarrow \mathrm{O_2} + \cancel{\mathrm{ClO}}$$
$$\cancel{\mathrm{ClO}} + \cancel{\mathrm{O}} \longrightarrow \cancel{\mathrm{Cl}} + \mathrm{O_2}$$

overall:

$$2\,\mathrm{O_3} \longrightarrow 3\,\mathrm{O_2}$$

Intermediates: O, ClO (both are made and then used up in a later step)

Catalyst: Cl (used in step 2 and reformed in step 3)

b.

$$\mathrm{O_3} \xrightarrow{sunlight} \mathrm{O_2} + \cancel{\mathrm{O}}$$
$$\mathrm{O_3} + \cancel{\mathrm{NO}} \longrightarrow \cancel{\mathrm{NO_2}} + \mathrm{O_2}$$
$$\cancel{\mathrm{NO_2}} + \cancel{\mathrm{O}} \longrightarrow \cancel{\mathrm{NO}} + \mathrm{O_2}$$

overall:

$$2\,\mathrm{O_3} \longrightarrow 3\,\mathrm{O_2}$$

Intermediates: O, $\mathrm{NO_2}$

Catalyst: NO

Exercise $6.E.31$***

a. In comparing trials 1 and 2, we see that $[\mathrm{NO}]$ is constant. The $[\mathrm{H_2}]$ doubles, as does the rate, so the reaction is of first order with respect to $\mathrm{H_2}$.

In comparing trials 3 and 4, the $[\mathrm{H_2}]$ is constant. The $[\mathrm{NO}]$ doubles, while the rate increases by a factor of 4, so the reaction is of second order with respect to NO.

b. rate = $k[\mathrm{NO}]^2[\mathrm{H_2}]$

c. Using the data from Trial 1:

$$rate = k[\mathrm{NO}]^2[\mathrm{H_2}]$$

$$k = \frac{rate}{[\mathrm{NO}]^2[\mathrm{H_2}]} = \frac{1.8 \times 10^{-4} M/min}{(0.0060M)^2(0.0010M)} = 5000 M^{-2} min^{-1}$$

d.

$$rate = k[\mathrm{NO}]^2[\mathrm{H_2}] = 5000 M^{-2} min^{-1}(0.0015M)^2(0.0035M) = 3.9 \times 10^{-5} M/min$$

e. The overall reaction described by the mechanism matches the reaction:

$$2\,\mathrm{NO}(g) + 2\,\mathrm{H_2}(g) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{H_2O}(g)$$

The rate law is based on the slow step:

rate = $k_2[\mathrm{N_2O_2}][\mathrm{H_2}]$

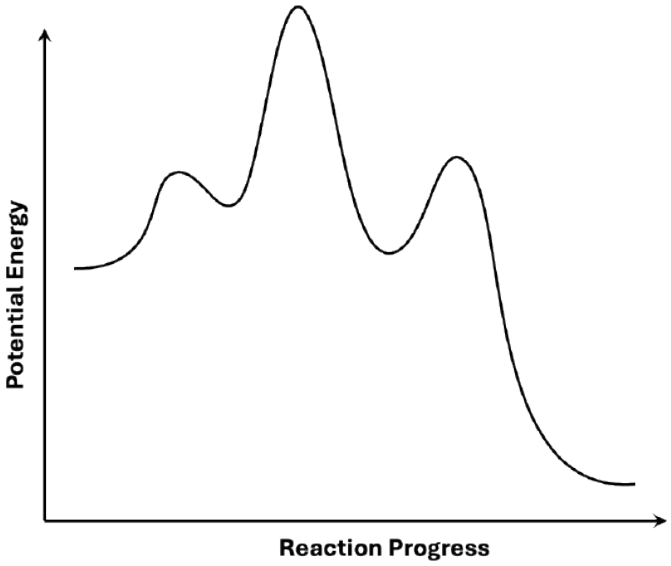
$\mathrm{N_2O_2}$ is an intermediate, so we need to use step 1 to write in terms of reactants.

$rate_{for} = rate_{rev}$

$k_1[\mathrm{NO}]^2 = k_{-1}[\mathrm{N_2O_2}]$ $[\mathrm{N_2O_2}]=k_1/k_{-1}[\mathrm{NO}]^2$

rate = $k_1k_2/k_{-1}[\mathrm{NO}]^2[\mathrm{H_2}]$ This matches the experimentally determined rate law.

Exercise $6.E.32$**



The reaction energy diagram should have three peaks to represent the transition states for the three steps in the mechanism. The activation energy of the second step should be the largest because it is the slow (rate-determining) step. The first and third steps are fast, so their activation energies are relatively low. In particular, the first step is a fast equilibrium, which means the activation energy is low in both the forward and reverse directions. The products should be lower in energy than the reactants because the overall reaction is exothermic.

Exercise $6.E.33$***

Find the activation energy by using the Arrhenius equation with the data from trials 1 and 2:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = \frac{-R \cdot \ln\left(\frac{2.42\times10^{-6}}{6.23\times10^{-7}}\right)}{\left(\frac{1}{575} - \frac{1}{555}\right)} = \frac{-8.314\ \mathrm{J/mol{\cdot}K} \cdot \ln(3.884)}{-6.238 \times 10^{-5}\ \mathrm{K^{-1}}} = 1.80 \times 10^5\ \mathrm{J/mol}$$

$$E_a = 180\ \mathrm{kJ/mol}$$

We can find the rate constant at 700 K by using the Arrhenius equation once again, now with the calculated value of the activation energy. Here, trials 1 and 3 are compared, but the same procedure can be done for trials 2 and 3:

$$\ln\left(\frac{k_3}{6.23 \times 10^{-7}}\right) = -\frac{1.80 \times 10^5\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol{\cdot}K}}\left(\frac{1}{700} - \frac{1}{555}\right)$$

$$\ln\left(\frac{k_3}{6.23 \times 10^{-7}}\right) = 8.08$$

$$\frac{k_3}{6.23 \times 10^{-7}} = e^{8.08} = 3229$$

$$k_3 = 6.23 \times 10^{-7} \times 3229 = 2.01 \times 10^{-3}\ \mathrm{M^{-1}s^{-1}}$$

Exercise $6.E.34$***

a. 2W + 2X ⟡ Y + Z

b. The slow step is rate-determining, so step 2.

c. The rate law is based on the slow step:

rate = k_2[A][X]

A is an intermediate, so we need to use step 1 to write in terms of reactants.

$rate_{for} = rate_{rev}$

$k_1[W]^2 = k_{-1}[A]$ $[A]=k_1/k_{-1}[W]^2$

$rate = k_1k_2/k_{-1}[W]^2[X]$

d. Doubling [W] would increase the rate by a factor of 4. Halving [X] would halve the rate. Together, these changes would cause the rate to double.

Exercise $6.E.35$**

$rate = k[I^-]^m[OCl^-]^n$

In comparing Trials 1 and 2 the $[OCl^-]$ is constant. The $[I^-]$ doubles and rate also doubles, so the reaction is first order with respect to I^-. m = 1.

We cannot "cross out" [\\(I^-]\\) to find n because no two trials have the same concentration of I^-. In order to find the reaction order for we need to use m = 1.

$$\frac{rate_1}{rate_3} = \frac{(0.10M)^1(0.050M)^n)}{(0.30M)^1(0.010M)^n)} = \frac{3.05 \times 10^{-4}M/s}{1.83 \times 10^{-4}M/s}$$

$$\frac{1}{3}(5^n) = 1.6666667$$

$$5^n = 5$$

$$n = 1$$

$$rate = k[OCl^-][I^-]$$

$$3.05 \times 10^{-4}M/s = k(0.05M)(0.10M)$$

$$k = 6.1 \times 10^{-2}M^{-1}s^{-1}$$

Exercise $6.E.36$**

For a first-order reaction, the integrated rate law is $ln\frac{[A]_t}{[A]_0} = -kt$

For the half-life, $t = t_{1/2}$, $[A]_t = 0.5[A]_0$. With $k=5.95 \times 10^{-4}\ s^{-1}$:

$$ln\left(\frac{0.5[A]_0}{[A]_0}\right) = -(5.95 \times 10^{-4}s^{-1})t_{1/2}$$

$t_{1/2}$ = 1165 s

$$1165s\left(\frac{1min}{60s}\right)\left(\frac{1h}{60min}\right) = 0.324h$$

To find amount remaining after 0.75 h, first convert to s:

$$0.75h\left(\frac{60min}{1h}\right)\left(\frac{60s}{1min}\right) = 2700s$$

$$ln\frac{[A]_t}{[A]_0} = -(5.95 \times 10^{-4}s^{-1})(2700s) = 1.61$$

$$\frac{[A]_t}{[A]_0} = e^{-1.61} = 0.20$$

This means that the $[A]_{0.75h}=0.20[A]_0$ which means that 20% of the cyclopropane remains after 0.75 h.

Video solution

Exercise $6.E.37$**

Because step ii is the slow step, it is the rate-determining step, and the rate law should be derived according to it.

$rate = k_2[Br][H_2]$

Br is an intermediate, so we need to find an expression for [Br] in terms of reactants by using the first fast equilibrium step:

$rate_{for} = rate_{rev}$

$k_1[Br_2] = k_{-1}[Br]^2$, $[Br] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Br_2]^{1/2}$

We can now replace [Br] in the original rate law expression, giving:

$rate = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}$

Exercise $6.E.38$**

$rate = k[A]^2[B]^0 = k[A]^2 = 0.0107\ M^{-1}\ min^{-1}(0.0010M)^2 = 1.07 \times 10^{-8}$ M/min

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7: EQUILIBRIUM FUNDAMENTALS

7.1: Introduction

7.2: The Dynamic Nature of Equilibria

7.3: Reactant Quotients and Equilibrium Constants

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7.E: Equilibrium Fundamentals (Exercises)

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7.1: Introduction

Equilibrium by Design: Self-Assembled Monolayers

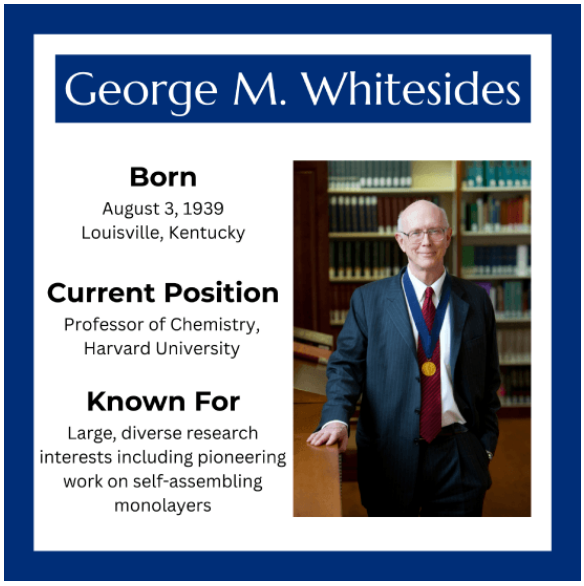


Figure 7.1.1**:** A graphic with basic facts about George M. Whitesides, American chemist who pioneered the field of self-assembled monolayer (SAM) technology. This unique phenomenon has now been studied in-depth for different molecules and surfaces, finding applications in biosensors, microelectronics, and tissue engineering. Image from Wikimedia Commons with permission under Creative Commons license CC-BY.

Chemical equilibrium occurs when the forward and reverse rates of a reversible process are equal, resulting in a stable mixture of products and reactants. While we often study equilibrium in the context of chemical reactions, it also plays an important role in how molecules behave at surfaces. For Dr. George M. Whitesides, a pioneer in nanoscience and surface chemistry, equilibrium became a powerful tool for building new materials.

In the 1980s, Whitesides and his team developed a technique to create self-assembled monolayers (SAMs): ultrathin films made of molecules that spontaneously organize themselves into ordered layers on surfaces. These layers form through reversible processes, where molecules temporarily stick to a surface and sometimes detach again. Over time, a balance is reached between molecules attaching and leaving, a state known as adsorption equilibrium. Once this dynamic balance is established, other interactions, such as covalent bonding and intermolecular forces, stabilize the arrangement both between the molecules and between the molecules and the surface. Under the right conditions, the molecules align with remarkable precision, creating a well-ordered layer through the interplay of reversible and stabilizing forces at the nanoscale.

What makes this system remarkable is not just the self-assembly itself, but how it can be harnessed to create functional materials. By modifying the chemical groups on the surface, Whitesides and his team designed SAMs that interact selectively with proteins or cells, enabling precise molecular recognition. Some SAMs can even prevent fouling, a common problem in biological systems where random proteins stick to surfaces and interfere with detection. These capabilities have made SAMs valuable tools in biosensors, microelectronics, and tissue engineering.

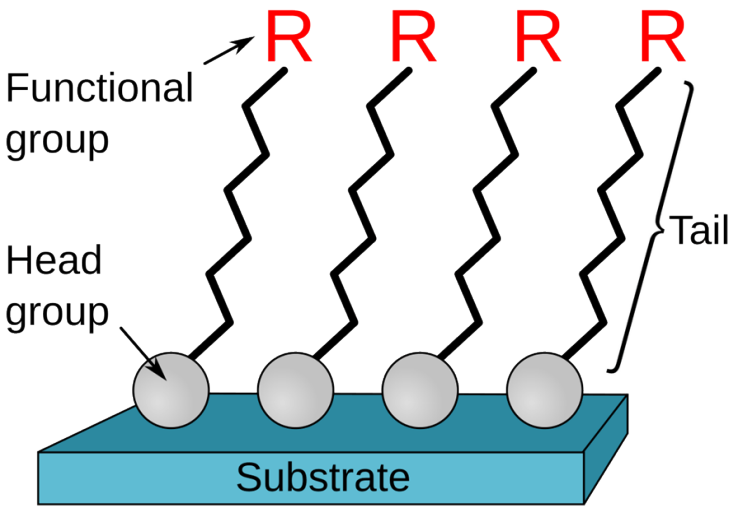


Figure 7.1.2**:** A schematic diagram of a basic self-assembled monolayer (SAM). Molecules that are optimal for SAM formation often pos
head group, a tail, and a functional group. The head group, also often called the anchoring group, allows the molecule to bind to the surf
that it orients itself in a specific way; for example, SAMs on gold surfaces use thiol groups ($-\mathrm{SH}$). The tail group, also called a linker, co
the head group to the functional group and creates stability in the SAM via covalent bonds or intermolecular forces between the tail gr
The functional group is what allows for the specific attachment or recognition of different biomolecules or cells. Image reprinted fr
Wikimedia Commons, with permission under open access license CC-BY.

By applying equilibrium principles to build SAMs, Whitesides was able to design functional materials with real-world applications, revolutionizing the field of surface chemistry. In this chapter, you'll explore the core principles of chemical equilibrium, including how reversible reactions behave, how systems respond to changes, and how to apply that information.

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7.2: The Dynamic Nature of Equilibria

Learning Objective

- Describe the dynamic nature of a chemical equilibrium

A standard convention for writing chemical equations is to place reactant formulas on the left side of a reaction arrow and product formulas on the right. By this convention (and the definitions of “reactant” and “product”), a chemical equation is understood to proceed from left to right. However, many reactions are reversible and may proceed in both the forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and products stop changing, and the system is said to be at equilibrium. The relative amounts of reactants and products at equilibrium can vary: some equilibrium mixtures contain predominantly products, some contain predominantly reactants, and others contain appreciable amounts of both.

Figure 7.2.1 illustrates these fundamental concepts using the reversible decomposition of colorless dinitrogen tetroxide ($\mathrm{N_2O_4\,(g)}$) into brown nitrogen dioxide ($\mathrm{NO_2\,(g)}$):

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons 2\ \mathrm{NO_2\,(g)}$$

Note that a special double arrow (⇌) is used to emphasize the reaction’s reversible nature.

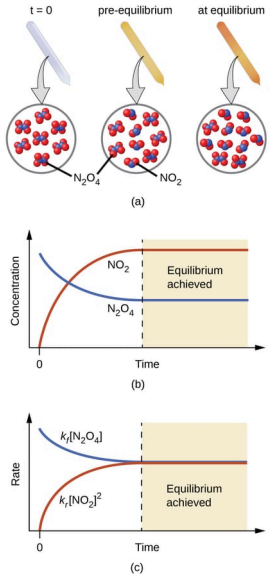


Figure 7.2.1: (a) A sealed tube containing colorless $\mathrm{N_2O_4}$ darkens as it decomposes to yield brown $\mathrm{NO_2}$. (b) Plot of concentration vs. time as the decomposition reaction proceeds to equilibrium. At equilibrium, the concentrations of the reactants and the products no longer change. (c) Plot of rate vs. time as the decomposition reaction proceeds to equilibrium. At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, the rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\mathrm{rate}_f = k_f\,[N_2O_4]$$

$$\mathrm{rate}_{\ r} = k_r\,[NO_2]^2$$

At the start of the reaction (t = 0), there is only $\mathrm{N_2O_4}$ (the reactant) present and no $\mathrm{NO_2}$ (the product) is present. At this point, the forward reaction proceeds at a certain rate, but the reverse reaction cannot occur yet because there is no $\mathrm{NO_2}$. As time passes,

N_2O_4 is consumed, so its concentration decreases, while NO_2 is formed, causing its concentration to increases (see Figure $7.2.1b$). As the N_2O_4 concentration gets lower, the rate of the forward reaction decreases; at the same time, the increasing concentration of NO_2 speeds up the reverse reaction (see Figure $7.2.1c$). This continues until the rates of the forward and reverse reactions become equal. At this point, the reaction has reached equilibrium, and the concentrations of N_2O_4 and NO_2 remain constant (shaded areas of Figure $7.2.1b$ and Figure $7.2.1c$).

Even at equilibrium, the reaction does not stop. Both the forward and reverse reactions continue at the same rate. Because the forward and reverse processes occur simultaneously and continuously, we describe equilibrium as dynamic. This dynamic nature of equilibrium is a key concept in understanding how chemical reactions behave and will be explored further in this chapter and subsequent chapters.

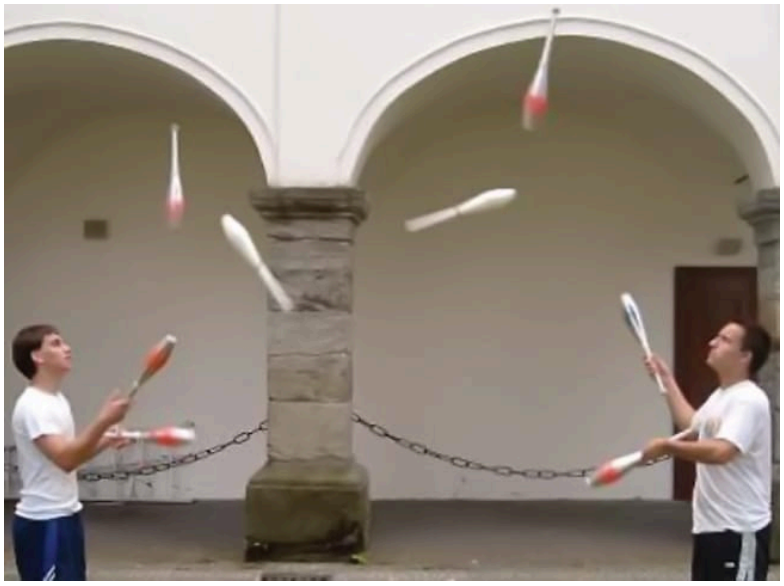


Figure $7.2.2$: A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

Physical changes, such as phase transitions, are also reversible and can establish equilibria. Consider the vaporization of bromine:

$$\mathrm{Br_2\,(l)} \rightleftharpoons \mathrm{Br_2\,(g)}$$

When liquid bromine is added to an empty container and sealed, vaporization (the forward process) proceeds at a roughly constant rate as long as the temperature and exposed surface area of the liquid remain constant. As more bromine vapor is produced, the reverse process (condensation) becomes faster. Eventually, the rates of vaporization and condensation become equal, and the system reaches equilibrium. At this point, the pressure of $\mathrm{Br_2\,(g)}$ in the container remains constant.

A photograph showing the sealed tube at equilibrium is shown in Figure $7.2.3$.



Figure 7.2.3: A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

Summary

Chemical equilibrium occurs when the rates of the forward and reverse reactions are equal, resulting in constant concentrations of reactants and products. Equilibrium is dynamic, meaning that both reactions continue to occur at the same rate. Equilibrium concepts apply to both chemical reactions and physical processes, such as phase changes.

Glossary

chemical 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
: A chemical reaction that can proceed in both the forward and reverse directions under given conditions.

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7.3: Reactant Quotients and Equilibrium Constants

Learning Objectives

- Write expressions for and calculate the reaction quotient, Q, and the equilibrium constant, K, in terms of concentrations and pressures
- Use the reaction quotient (Q) to predict the direction of reaction
- Interpret the magnitude of an equilibrium constant (K) to determine to the extent of reaction at equilibrium
- Relate K_p to K_c for gas-phase reactions
- Calculate K for related reactions by applying rules for reversing, scaling, and combining equilibrium constants.

Definition of Chemical Equilibria

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the reaction in the previous section, the decomposition of $\mathrm{N_2O_4}$:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)}$$

Both the forward and reverse reactions consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4]$$

and

$$\text{reverse rate} = k_r[NO_2]^2$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

This expression demonstrates the fundamental relationship between chemical kinetics and chemical equilibrium. Under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

The reaction involving $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ is a reversible elementary reaction and so the connection between kinetics and equilibrium is clear. It turns out that the equilibrium constant, K, defined here can be applied to all reactions whether elementary or overall.

For a general reversible reaction:

$$mA + nB + \rightleftharpoons xC + yD$$

the equilibrium constant in terms of molar concentrations (K_c) is:

$$K_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

If the reactants and products are gaseous, a similar expression can use either concentrations or partial pressures (K_p):

$$K_p = \frac{P_C^x P_D^y}{P_A^m P_B^n}$$

The magnitude of the equilibrium constant (K) reflects the composition of the reaction mixture at equilibrium and indicates how far the reaction proceeds in the forward direction.

- A large K (much greater than 1) means most reactants are converted into products by the time equilibrium is reached.
- A small K (much less than 1) means only a small portion of reactants are converted into products at equilibrium.

It is important to note that K does not indicate the speed of the reaction. Some reactions reach equilibrium almost instantly, while others take hours, days, or even years.

Example 7.3.1: Writing Equilibrium Constant Expressions

Write the concentration-based equilibrium constant expression for each of the following reactions:

a. $3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)$
b. $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$
c. $4\,NH_3\,(g) + 7\,O_2\,(g) \rightleftharpoons 4\,NO_2\,(g) + 6\,H_2O\,(g)$

Solution

a. $$K_c = \frac{[O_3]^2}{[O_2]^3}$$

b. $$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

c. $$K_c = \frac{[NO_2]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^7}$$

Exercise 7.3.1

Write the concentration-based equilibrium constant expression for each of the following reactions:

a. $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$
b. $C_4H_8\,(g) \rightleftharpoons 2\,C_2H_4\,(g)$
c. $2\,C_4H_{10}\,(g) + 13\,O_2\,(g) \rightleftharpoons 8\,CO_2\,(g) + 10\,H_2O\,(g)$

Answer available at the end of this section.

Units of K and Chemical Activity

All equilibrium constants (K) are unitless. This is because chemical equilibrium does not relate to simple concentrations or pressures, but to chemical activity, a. Chemical activity is essentially an "effective concentration" that reflects not only the number of particles per unit volume, but also moderating effects such as attractions and repulsions between molecules.

Chemical activity is unitless because it is defined relative to a standard state. For example, the activity of chemical A (a_A) in an aqueous solution is described by the concentration of A in the aqueous phase ($[A]$) relative to its concentration at standard state ($[A]_{ss}$), which is defined as 1.0 M. The activity relationship also includes an activity coefficient (γ) that represents the sum of all moderating effects:

$$a_A = \gamma \frac{[A]}{[A]_{ss}}$$

Activity is discussed in depth in more rigorous treatments of chemical equilibrium. In most scenarios, and all scenarios discussed in CHM 135H, concentration or partial pressure is a reasonable proxy for activity ($\gamma \approx 1$) and so we will use concentration or pressure in all of our equilibrium calculations:

$$a_A \approx [A]$$

We are introducing the concept of chemical activity here to explain why equilibrium constants are unitless. This concept will also be useful in certain discussions later in CHM 135H, but it will not be covered in depth in this course.

Reaction Quotients

The reaction quotient Q has the same format as the equilibrium constant K, but instead of describing the equilibrium position of the reaction it describes current reaction conditions. As a reaction proceeds, the value of Q changes. Eventually, the system reaches a point where Q becomes constant, indicating that the reaction has reached equilibrium, where,

$$K = Q \text{ (at equilibrium)}$$

To illustrate, consider the the following reaction under two different starting conditions:

$$2\,\mathrm{SO_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{SO_3\,(g)}$$

The reaction quotient, as defined by concentration, is described by the following expression:

$$Q_c = \frac{[\mathrm{SO_3}^2]}{[\mathrm{SO_2}^2][\mathrm{O_2}]}$$

- **Starting with only reactants** $\mathrm{SO_2}$ **and** $\mathrm{O_2}$ Figure 7.3.1 (a)**:**
  Initially, $[\mathrm{SO_3}] = 0$, so $Q_c = 0$. As the reaction proceeds in the forward direction, $[\mathrm{SO_3}]$ increases and $[\mathrm{SO_2}]$ and $[\mathrm{O_2}]$ decrease, causing Q_c to increase until it stops changing at equilibrium.
- **Starting with only the product** $\mathrm{SO_3}$ Figure 7.3.1 (b)**:**
  Initially, $[\mathrm{SO_2}] = [\mathrm{O_2}] = 0$, so Q_c is essentially infinite (∞). As the reaction proceeds in the reverse direction, $[\mathrm{SO_3}]$ decreases and $[\mathrm{SO_2}]$ and $[\mathrm{O_2}]$ increase, causing Q_c to decrease until it becomes constant at equilibrium.

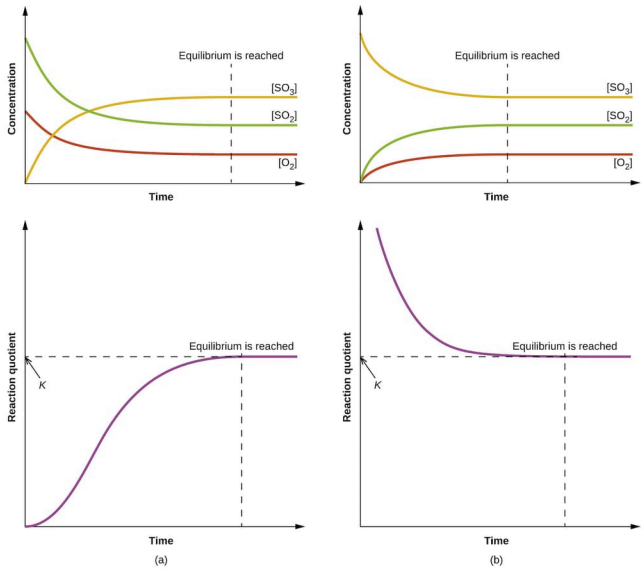


Figure 7.3.1 Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

In the example shown in Figure 7.3.1 a comparison between Q and K can be used to predict the net direction of the reaction.

A reaction will proceed in the direction that moves it toward equilibrium:

- If $Q < K$ (7.3.1(a)) the forward reaction is favoured and products will be formed as the reaction proceeds towards equilibrium
- If $Q > K$ (7.3.1(b)) the reverse reaction is favoured and reactants will be formed as the reaction proceeds towards equilibrium
- If $Q = K$, the system is already at equilibrium and no net reaction will take place

Experimental observations show that K is always the same for a given reaction at a particular temperature, a principle known as the law of mass action. This is illustrated in Figure 7.3.1 where both initial conditions lead to the same value for the equilibrium constant.

Example 7.3.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

When 0.10 mol NO_2 is added to a 1.0 L flask at 25 °C, the concentration changes so that at equilibrium, [NO_2] = 0.016 *M* and [N_2O_4] = 0.042 *M*.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

(a) Before any product is formed

$$[NO_2] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\text{ M}$$

$$[N_2O_4] = 0\text{ M}$$

Thus

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium,

$$K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Exercise 7.3.2

For the reaction

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

the equilibrium concentrations are [SO_2] = 0.90 *M*, [O_2] = 0.35 *M*, and [SO_3] = 1.1 *M*. What is the value of the equilibrium constant, K_C?

Answer available at the end of this section.

A comparison of Q versus K is a fundamental concept that will underpin the remainder of the course, so let's consider another example using the following reversible reaction:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) \quad K_c = 0.640 \quad T = 800^\circ C$$

Three experiments were performed with different initial conditions. In each case, the reaction proceeds in the direction necessary to reach equilibrium, where K_c = 0.640.

1. **Experiment 1: Starting with Only Reactants**
   Initial concentrations: [CO] = [H_2O] = 0.0243 M, [CO_2] = [H_2] = 0 M

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0)(0)}{(0.0243)(0.0243)} = 0.00$$

   Since $Q_c < K_c$, the reaction proceeds in the forward direction towards products until equilibrium is reached.

   At equilibrium the following concentrations were observed: [CO] = [H_2O] = 0.0135 M, [CO_2] = [H_2] = 0.0108 M

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0108M)(0.0108M)}{(0.0135M)(0.0135M)} = 0.640$$

2. **Experiment 2: Starting with only products**
   Initial concentrations: [CO] = [H_2O] = 0 M, [CO_2] = [H_2] = 0.0468 M

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0468)(0.0468)}{(0)(0)} = \infty$$

   Since $Q_c > K_c$, the reaction proceeds in the reverse direction towards reactants.

   At equilibrium the following concentrations were observed: [CO] = [H_2O] = 0.0260 M, [CO_2] = [H_2] = 0.0208 M

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0208M)(0.0208M)}{(0.0260M)(0.0260M)} = 0.640$$

3. **Experiment 3: A Mixture of Reactants and Products**
   Initial concentrations: [CO] = 0.0400 M, [H_2O] = 0.0500 M, [CO_2] = 0.0100 M, [H_2] = 0.00400 M

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 0.0200$$

   Since $Q_c < K_c$, the reaction proceeds in the forward direction towards products until equilibrium is reached.

   At equilibrium the following concentrations were observed: [CO] =0.0240 M [H_2O] = 0.0340 M, [CO_2] = 0.0260 M, [H_2] = 0.0200 M

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} \frac{(0.0260M)(0.0200M)}{(0.0240M)(0.0340M)} = 0.640$$

In Experiments 1 and 3, Q_c was initially less than K_c, so the reactions proceed forward to produce more products. In Experiment 2, Q_c was initially greater than K_c, so the reaction proceed in reverse to produce more reactants.

In all cases, the system reaches the same equilibrium constant (K_c), though the final equilibrium concentrations differ.

Example 7.3.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)} \quad K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.020 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.020 *M*	0.0011 *M*	0.0025 *M*

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040$$

$Q_c < K_c$ (0.040 < 0.64)

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will proceed in the forward direction.

Exercise 7.3.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

a. A 1.00-L flask containing 0.0500 mol of $NO\,(g)$, 0.0155 mol of $Cl_2\,(g)$, and 0.500 mol of $NOCl$:

$$2\,NO\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NOCl\,(g) \quad K_c = 4.6 \times 10^4$$

b. A 2.00-L flask containing 230 g of $SO_3\,(g)$:

$$2\,SO_3\,(g) \rightleftharpoons 2\,SO_2\,(g) + O_2\,(g) \quad K_c = 0.230$$

Answer available at the end of this section.

Homogeneous and Heterogeneous Equilibria

A homogeneous equilibrium occurs when all reactants and products are in the same phase. This is common in solutions, particularly in aqueous and gas-phase equilibria. For reactions in aqueous solution, the equilibrium constant expression is based on the concentrations of dissolved species:

$$\mathrm{C_2H_2\,(aq) + 2\,Br_2\,(aq) \rightleftharpoons C_2H_2Br_4\,(aq)} \qquad K_c = \frac{[\mathrm{C_2H_2Br_4}]}{[\mathrm{C_2H_2}]\,[\mathrm{Br_2}]^2}$$

$$\mathrm{I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3{}^-\,(aq)} \qquad K_c = \frac{[\mathrm{I_3{}^-}]}{[\mathrm{I_2}]\,[\mathrm{I^-}]}$$

$$\mathrm{HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)} \qquad K_c = \frac{[\mathrm{H_3O^+}]\,[\mathrm{F^-}]}{[\mathrm{HF}]}$$

$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4{}^+\,(aq) + OH^-\,(aq)} \qquad K_c = \frac{[\mathrm{NH_4{}^+}]\,[\mathrm{OH^-}]}{[\mathrm{NH_3}]}$$

In the last two examples, water is a reactant, but its concentration is not included in the equilibrium expression. This is because, as discussed above, equilibrium constants (K) and reaction quotients (Q) are based on chemical activity (a) with concentration or pressure used as a reasonable proxy. The chemical activity of all pure liquids and solids is by definition 1:

$$a_{liquid} = 1$$

$$a_{solid} = 1$$

For liquids and solids, their density does not appreciably change, so their effective concentration relative to standard state (1 M for liquids, standard density for solids) remains 1, making their activity exactly 1. Because of this, all pure liquids and solids are omitted from equilibrium and reaction quotient expressions.

A heterogeneous equilibrium involves reactants and products in two or more different phases, as illustrated by the following examples:

$$\mathrm{PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,Cl^-\,(aq)} \qquad K_c = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2$$

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightleftharpoons CaCO_3\,(s)} \qquad K_c = \frac{1}{[\mathrm{CO_2}]} \qquad K_p = \frac{1}{P_{\mathrm{CO_2}}}$$

$$\mathrm{C\,(s) + 2\,S\,(g) \rightleftharpoons CS_2\,(g)} \qquad K_c = \frac{[\mathrm{CS_2}]}{[\mathrm{S}]^2} \qquad K_p = \frac{P_{\mathrm{CS_2}}}{P_{\mathrm{S}}^2}$$

$$\mathrm{Br_2\,(l) \rightleftharpoons Br_2\,(g)} \qquad K_c = [\mathrm{Br_2}] \qquad K_p = P_{\mathrm{Br_2}}$$

Consistent with the discussion above, only gases and solutes appear in the equilibrium expression. For reactions involving gases, equilibrium constants can be defined in terms of concentration (K_c) or partial pressure (K_p).

Gas Mixtures and K_c vs. K_p

Any gas can be defined by either its concentration ($M = \frac{mol}{L} = \frac{n}{V}$) or pressure ($P$). The relationship between these two units can be derived from the ideal gas law:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = MRT$$

where P is partial pressure, n is the number of moles present, V is volume, R is the gas constant, T is temperature, and M is the concentration of the gas in mol/L.

Let's explore the relationship between K_c and K_p using this general gas phase reaction:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

Let's first define the equilibrium constant in terms of partial pressures (K_p):

$$K_P = \frac{(P_C)^c\,(P_D)^d}{(P_A)^a\,(P_B)^b}$$

Then transform the expression into K_c by substitute $P = MRT$ for each of the reactants and products:

$$K_P = \frac{([C] \times RT)^c([D] \times RT)^d}{([A] \times RT)^a([B] \times RT)^b}$$

Finally, group the concentration and RT terms together to define the relationship between K_p and K_c:

$$\begin{aligned} K_P &= \frac{[C]^c[D]^d}{[A]^a[B]^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}} \\ &= K_c(RT)^{(c+d)-(a+b)} \\ K_P &= K_c(RT)^{\Delta n} \end{aligned}$$

where Δn is the difference in the number of moles product and reactant gases:

$$\Delta n = (c + d) - (a + b)$$

This equation is useful for converting between equilibrium constants based on concentration and partial pressure. The value of Δn determines how the values of K_p and K_c relate to each other.

Example 7.3.4: Calculation of K_P

Write the equations relating K_c to K_p for each of the following reactions:

a. $\mathrm{C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)}$
b. $\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)}$
c. $\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$

Solution

a. $\Delta n = (2) - (1) = 1$

$$K_P = K_c(RT)^{\Delta n} = K_c(RT)^1 = K_c(RT)$$

b. $\Delta n = (2) - (2) = 0$

$$K_P = K_c(RT)^{\Delta n} = K_c(RT)^0 = K_c$$

c. $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c(RT)^{\Delta n} = K_c(RT)^{-2} = \frac{K_c}{(RT)^2}$$

Example 7.3.5

K_C is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2\,(g) + 4\,H_2\,(g) \rightleftharpoons CH_4\,(g) + 2\,H_2S\,(g)}$$

What is K_P at this temperature?

Solution

$$K_p = K_c(RT)^{\Delta n} = (0.28)[(0.08206)(1173)]^{-2} = 3.0 \times 10^{-5}$$

Exercise 7.3.4

Write the equations relating K_C to K_P for each of the following reactions:

a. $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$
b. $N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$
c. $C_3H_8\,(g) + 5\,O_2\,(g) \rightleftharpoons 3\,CO_2\,(g) + 4\,H_2O\,(g)$

Answer available at the end of this section.

Exercise 7.3.5

At 227 °C, the following reaction has K_C = 0.0952:

$$CH_3OH\,(g) \rightleftharpoons CO\,(g) + 2\,H_2\,(g)$$

What is the value of K_P at this temperature?

Answer available at the end of this section.

Combining Equilibrium Constants

The equilibrium systems discussed so far have been relatively simple, involving a single reversible reaction. However, many chemical equilibria involve multiple related reactions that share reactants or products. In such cases, the equilibrium constant for the overall reaction can be determined by combining the equilibrium constants of the individual steps.

The following three rules describe how equilibrium constants are combined.

1. **Reversing a reaction**: If a reaction is reversed, the new equilibrium constant is the reciprocal of the original equilibrium constant:

$$A \rightleftharpoons B \quad K_c = \frac{[B]}{[A]}$$
$$B \rightleftharpoons A \quad K_c{}' = \frac{[A]}{[B]}$$
$$K_c{}' = \frac{1}{K_c}$$

2. **Changing stoichiometric coefficients**: If a reaction's stoichiometric coefficients are multiplied by a factor x, the equilibrium constant is raised to the power of x:

$$A \rightleftharpoons B \qquad K_c = \frac{[B]}{[A]}$$
$$xA \rightleftharpoons xB \quad K_c{}' = \frac{[B]^x}{[A]^x}$$
$$K_c{}' = K_c{}^x$$

3. **Adding reactions together**: If two or more reactions are added together, the overall equilibrium constant is the product of the individual equilibrium constants:

$$A \rightleftharpoons B \quad K_{c(1)} = \frac{[B]}{[A]}$$
$$B \rightleftharpoons C \quad K_{c(2)} = \frac{[C]}{[B]}$$

The net reaction is obtained by summing the two equations and cancelling any common species:

$$A + B \rightleftharpoons B + C$$
$$A + \cancel{B} \rightleftharpoons \cancel{B} + C$$
$$A \rightleftharpoons C$$

The equilibrium constant for the net reaction is:

$$K_c{}' = \frac{[C]}{[A]}$$

To confirm this relationship, we multiply the equilibrium constants of the individual steps:

$$K_{c(1)}K_{c(2)} = \frac{[B]}{[A]} \times \frac{[C]}{[B]} = \frac{\cancel{[B]}\,[C]}{[A]\,\cancel{[B]}} = \frac{[C]}{[A]} = K_c{}'$$

Thus, for any reaction obtained by adding multiple steps together, the equilibrium constant is:

$$K_c{}' = K_{c(1)}K_{c(2)}$$

Example 7.3.6: Equilibrium Constants for Coupled Reactions

For the following equilibrium:

$$2\,\mathrm{NH_3\,(g)} + 3\,\mathrm{I_2\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + 6\,\mathrm{HI\,(g)}$$

use the information below to calculate K_c for this reaction.

$$\mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)} \rightleftharpoons 2\,\mathrm{NH_3\,(g)} \quad K_{c(1)} = 0.50 \text{ at } 400^\circ C$$
$$\mathrm{H_2\,(g)} + \mathrm{I_2\,(g)} \rightleftharpoons 2\,\mathrm{HI\,(g)} \quad K_{c(2)} = 50 \text{ at } 400^\circ C$$

Solution

The equilibrium equation of interest and its K_c value may be derived from the equations for the two coupled reactions:

1. Reverse the first coupled reaction equation:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \quad K_{c(1)}{}' = \frac{1}{K_{c(1)}} = \frac{1}{0.50} = 2.0$$

2. Multiply the second reaction by 3:

$$3H_2(g) + 3I_2(g) \rightleftharpoons 6HI(g) \quad K_{c(2)}{}' = {K_{c(2)}}^3 = 50^3 = 1.25 \times 10^5$$

3. Finally, add the two revised equations:

$$2\,\mathrm{NH_3\,(g)} + \cancel{3H2(g)} + 3\,\mathrm{I_2\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + \cancel{3H2(g)} + 6\,\mathrm{HI\,(g)}$$
$$2\,\mathrm{NH_3\,(g)} + 3\,\mathrm{I_2\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + 6\,\mathrm{HI\,(g)}$$
$$K_c = K_{c(1)}{}' \times K_{c(2)}{}' = (2.0)\left(1.2 \times 10^5\right) = 2.5 \times 10^5$$

Exercise 7.3.6

Use the provided information to calculate Kc for the following reaction at 550 °C:

$$\mathrm{H_2\,(g)} + \mathrm{CO_2\,(g)} \rightleftharpoons \mathrm{CO\,(g)} + \mathrm{H_2O\,(g)} \qquad K_c = ?$$
$$\mathrm{CoO\,(s)} + \mathrm{CO\,(g)} \rightleftharpoons \mathrm{Co\,(s)} + \mathrm{CO_2\,(g)} \qquad K_{c(1)} = 490$$
$$\mathrm{CoO\,(s)} + \mathrm{H_2\,(g)} \rightleftharpoons \mathrm{Co\,(s)} + \mathrm{H_2O\,(g)} \qquad K_{c(2)} = 67$$

Answer available at the end of this section.

Summary

The reaction quotient (Q) is the ratio of the concentrations or partial pressures of products to reactants, with each species raised to its stoichiometric coefficient. The concentrations of pure solids, pure liquids, and solvents are not included in the expression for Q. As the reaction progresses, Q changes until the system reaches equilibrium, at which point $Q = K$.

The equilibrium constant (K) has the same mathematical form as Q, but it uses equilibrium concentrations or pressures. Importantly, K is a constant at a given temperature, regardless of the initial amounts of reactants and products.

Comparing Q and K allows us to predict the net direction of the reaction:

- If \(Q
- If $Q > K$, the reaction proceeds in the reverse direction towards equilibrium
- If $Q = K$, the reaction is at equilibrium and there is no net movement in either direction

At equilibrium, Q is always equal to K however the exact concentration or pressure values for each reaction or product can vary based on initial conditions. It is also important to remember that equilibrium is dynamic and so the reaction does not stop but the rates of the forward and reverse reactions are equal.

For gaseous reactions, Q and K can be expressed in terms of concentrations (Q_c and K_c) or partial pressures (Q_p and K_p). The following expression can be used to convert between the two, where Δn is the difference in the number of moles product and reactant gases:

$$K_P = K_c(RT)^{\Delta n}$$

If a chemical equation is reversed or multiplied by a factor, the equilibrium constant changes accordingly:

- Reversing the equation → The new K is the reciprocal of the original K.
- Multiplying the equation by a factor x → The new K is the original K raised to the power of x.
- For a reaction that is the sum of multiple steps → The overall K is the product of the individual equilibrium constants.

Glossary

equilibrium constant (*K*)
: The value of the reaction quotient for a system at equilibrium.

heterogeneous equilibrium
: Equilibrium between reactants and products in different phases.

homogeneous equilibrium
: Equilibrium within a single phase.

K_c
: The equilibrium constant for reactions based on concentrations of reactants and products.

K_p
: The equilibrium constant for gas-phase reactions based on partial pressures of reactants and products.

law of mass action
: When a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant.

reaction quotient (Q)
: The ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation.

Answers

Exercise 7.3.1

a. $$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

b. $$K_c = \frac{[C_2H_4]^2}{[C_4H_8]}$$

c. $$K_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$$

Exercise 7.3.2

$$K_c = \frac{[SO_3{}^2]}{[SO_2{}^2][O_2]} = \frac{1.1^2}{(0.90)^2(0.35)} = 4.3$$

Exercise 7.3.3

(a) $Q_c = 6.45 \times 10^3$, forward. (b) $Q_c = 0$, forward.

Exercise 7.3.4

(a) $K_P = K_C(RT)^{-1}$; (b) $K_P = K_C(RT)$; (c) $K_P = K_C(RT)$

Exercise 7.3.5

$$K_p = K_c(RT)^{\Delta n} = (0.0952)[(0.08206)(500)]^2 = 160 = 1.60 \times 10^2$$

Exercise 7.3.6

$K_c = \frac{1}{K_{c(1)}} \times K_{c(2)} = \frac{1}{490}(67) = 0.14$

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7.4: Equilibrium Calculations

Learning Objectives

- Determine the changes in concentration or pressure that occur as a system approaches equilibrium.
- Calculate equilibrium concentrations or pressures using initial conditions and the equilibrium expression.
- Compute equilibrium constants (K_c or K_p) from equilibrium data.

This section explores equilibrium calculations, which are fundamental in many scientific and technological fields. One important application is in pharmaceutical science, particularly in drug development and administration. When a drug is ingested or injected, it often undergoes multiple chemical equilibria that influence its concentration in the body. Understanding the quantitative aspects of these equilibria is crucial for determining the correct dosage needed to achieve the desired therapeutic effect.

Equilibrium calculations focus on how reactant and product concentrations change as a system progresses from its initial state to equilibrium. These changes are directly related to the stoichiometry of the reaction. For example, consider the decomposition of ammonia:

$$2\,\mathrm{NH_3\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)}$$

Regardless of the initial amounts of reactants and products, the reaction will always follow the same stoichiometric relationships between changes in concentration, as dictated by the balanced equation.

For instance, if the nitrogen concentration increases by an amount x:

$$\Delta\,[N_2] = +x$$

then the corresponding changes in the other species concentrations are:

$$\Delta\,[\mathrm{H_2}] = \Delta\,[\mathrm{N_2}]\left(\frac{3\text{ mol }\mathrm{H_2}}{1\text{ mol }\mathrm{N_2}}\right) = +3x$$

$$\Delta\,[\mathrm{NH_3}] = -\Delta\,[\mathrm{N_2}]\left(\frac{2\text{ mol }\mathrm{NH_3}}{1\text{ mol }\mathrm{N_2}}\right) = -2x$$

The negative sign indicates a decrease in concentration. If nitrogen is being formed in the reaction and its concentration is increasing, ammonia must be reacting and its concentration must decrease accordingly.

Example 7.4.1: Determining Relative Changes in Concentration

For the following reactions, find the missing terms representing concentration changes for the reactants and products to reach equilibrium.

a. $\underset{x}{\mathrm{C_2H_2\,(g)}} + 2\,\underset{?}{\mathrm{Br_2\,(g)}} \rightleftharpoons \underset{?}{\mathrm{C_2H_2Br_4\,(g)}}$

b. $\underset{?}{\mathrm{I_2\,(aq)}} + \underset{?}{\mathrm{I^-\,(aq)}} \rightleftharpoons \underset{x}{\mathrm{I_3^-\,(aq)}}$

c. $\underset{x}{\mathrm{C_3H_8\,(g)}} + 5\,\underset{?}{\mathrm{O_2\,(g)}} \rightleftharpoons 3\,\underset{?}{\mathrm{CO_2\,(g)}} + 4\,\underset{?}{\mathrm{H_2O\,(g)}}$

Solution

a. $\underset{x}{\mathrm{C_2H_2\,(g)}} + 2\,\underset{2x}{\mathrm{Br_2\,(g)}} \rightleftharpoons \underset{-x}{\mathrm{C_2H_2Br_4\,(g)}}$

b. $$\underset{-x}{\mathrm{I_2\,(aq)}} + \underset{-x}{\mathrm{I^-\,(aq)}} \rightleftharpoons \underset{x}{\mathrm{I_3{}^-\,(aq)}}$$

c. $$\underset{x}{\mathrm{C_3H_8\,(g)}} + \underset{5x}{\mathrm{5\,O_2\,(g)}} \rightleftharpoons \underset{-3x}{\mathrm{3\,CO_2\,(g)}} + \underset{-4x}{\mathrm{4\,H_2O\,(g)}}$$

Exercise 7.4.1

For the following reactions, find the missing terms representing concentration changes for the reactants and products to reach equilibrium.

a. $$\underset{?}{\mathrm{2\,SO_2\,(g)}} + \underset{x}{\mathrm{O_2\,(g)}} \rightleftharpoons \underset{?}{\mathrm{2\,SO_3\,(g)}}$$

b. $$\underset{?}{\mathrm{C_4H_8\,(g)}} \rightleftharpoons \underset{-2x}{\mathrm{2\,C_2H_4\,(g)}}$$

c. $$\underset{?}{\mathrm{4\,NH_3\,(g)}} + \underset{-7x}{\mathrm{7\,O_2\,(g)}} \rightleftharpoons \underset{?}{\mathrm{4\,NO_2\,(g)}} + \underset{?}{\mathrm{6\,H_2O\,(g)}}$$

Answer available at the end of this section.

Calculation of an Equilibrium Constant

The equilibrium constant (K) for a reaction is determined using the equilibrium concentrations for K_c or partial pressures for K_p of its reactants and products. If these values are known, the calculation is straightforward: they are substituted into the equilibrium expression for K. However, in many cases, the equilibrium concentrations are not given directly and must be determined from the initial conditions. A systematic way to organize information for these types of problems is by using an ICE table.

An ICE table helps track how the system moves from its Initial concentrations (I) through the Changes (C) that occur as the reaction progresses to Equilibrium (E). It follows the stoichiometry of the reaction, making it easier to set up and solve equilibrium expressions.

Note: An ICE table is not a special formula but rather a structured way to apply the fundamental definition of equilibrium—a state in which the rates of the forward and reverse reactions are equal, and concentrations no longer change. It is a mathematical representation of what happens in all equilibrium reactions: the system starts from some initial conditions, undergoes changes as it approaches equilibrium, and reaches a final equilibrium state where the concentrations of reactants and products no longer change.

Example 7.4.2: Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$\mathrm{I_2\,(aq) + I^-\,(aq)} \rightleftharpoons \mathrm{I_3{}^-\,(aq)}$$

A solution with the initial concentrations of $\mathrm{I_2}$ and $\mathrm{I^-}$ of $1.000 \times 10^{-3}\ \mathrm{M}$ results in an equilibrium concentration of $\mathrm{I_2}$ of $6.61 \times 10^{-4}\ \mathrm{M}$. What is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, equilibrium concentrations are needed for all the reactants and products:

$$K_c = \frac{[\mathrm{I_3{}^-}]}{[\mathrm{I_2}]\,[\mathrm{I^-}]}$$

We are given the initial concentrations of the reactants and the equilibrium concentration of $\mathrm{I_2}$. Let's use this information to derive terms for the equilibrium concentrations of the species, presenting all the information in an ICE table where the change in concentrations are relate the stoichiometry of the reaction.

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x$	$-x$	$+x$
Equilibrium concentration (*M*)	$1.000 \times 10^{-3} - x$	$1.000 \times 10^{-3} - x$	x

At equilibrium the concentration of $\mathrm{I_2}$ is 6.61×10^{-4} M so that

$$\begin{aligned} 1.000 \times 10^{-3} - x &= 6.61 \times 10^{-4} \\ x &= 1.000 \times 10^{-3} - 6.61 \times 10^{-4} \\ &= 3.39 \times 10^{-4} M \end{aligned}$$

The ICE table may now be updated with numerical values for all its concentrations:

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the *K* expression and solve:

$$\begin{aligned} K_c &= \frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}]\,[\mathrm{I^-}]} \\ &= \frac{3.39 \times 10^{-4} M}{(6.61 \times 10^{-4} M)\,(6.61 \times 10^{-4} M)} = 776 \end{aligned}$$

Exercise 7.4.2

Consider the following reaction:

$$\mathrm{PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)}$$

0.480 atm of $\mathrm{PCl_3}$ and 0.400 atm of $\mathrm{Cl_2}$ gases are added to an empty flask. At equilibrium, the partial pressure of $\mathrm{PCl_5}$ is 0.320 atm. What is K_p for the reaction?

Answer available at the end of this section.

Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one of the equilibrium concentrations are known, the missing equilibrium concentration can be determined algebraically using the equilibrium expression. An example of this type of calculation is shown in the next example.

Example 7.4.3: Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the K_c for the reaction,

$$\mathrm{N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)}$$

is 4.1×10^{-4}. Calculate the equilibrium concentration of $\mathrm{NO\,(g)}$. The equilibrium concentrations of $\mathrm{N_2}$ and $\mathrm{O_2}$ at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

Substitute the provided quantities into the equilibrium constant expression and solve for [NO]:

$$\begin{aligned} K_c &= \frac{[NO]^2}{[N_2]\,[O_2]} \\ [NO]^2 &= K_c\,[N_2]\,[O_2] \\ [NO] &= \sqrt{K_c\,[N_2]\,[O_2]} \\ &= \sqrt{\left(4.1 \times 10^{-4}\right)(0.036)(0.0089)} \\ &= \sqrt{1.31 \times 10^{-7}} \\ &= 3.6 \times 10^{-4} \end{aligned}$$

[NO] is $3.6 \times 10^{-4}\ \mathrm{mol/L}$ at equilibrium under these conditions.

Exercise 7.4.3

The equilibrium constant K_c for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}.

$$\mathrm{2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)}$$

What is the equilibrium concentration of ammonia, $[\mathrm{NH_3}]$, if the equilibrium concentrations of nitrogen and hydrogen are 4.26 M and 2.09 M, respectively?

Answer available at the end of this section.

Calculation of Equilibrium Concentrations from Initial Concentrations

Let's now look at the calculation of equilibrium concentrations from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.
2. Set up an ICE table to organize initial concentrations, changes in concentration, and equilibrium concentrations.
3. Calculate the concentration changes based on stoichiometry and solve for the equilibrium concentrations.
4. Verify your results by substituting the calculated equilibrium concentrations into the equilibrium expression to check consistency with K.

The final two example exercises in this chapter demonstrate the application of this strategy in detail.

Example 7.4.4: Calculation of Equilibrium Concentrations

At a certain temperature, the equilibrium constant K_c for the decomposition of $\mathrm{PCl_5\,(g)}$ into $\mathrm{PCl_3\,(g)}$ and $\mathrm{Cl_2\,(g)}$ is 0.0211. What are the equilibrium concentrations of $\mathrm{PCl_5}$, $\mathrm{PCl_3}$, and $\mathrm{Cl_2}$ in a mixture that initially contained only $\mathrm{PCl_5}$ at a concentration of 1.00 M?

$$\mathrm{PCl_5\,(g)} \rightleftharpoons \mathrm{PCl_3\,(g) + Cl_2\,(g)}$$

Solution

Step 1.

Determine the direction the reaction proceeds.

Because only the reactant is present initially $Q_c = 0$ and the reaction will proceed to the right.

Step 2:

Set up an ICE table.

	$\mathrm{PCl_5} \rightleftharpoons$	$\mathrm{PCl_3}$ +	$\mathrm{Cl_2}$
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	x	x

Step 3.

Solve for the change and the equilibrium concentrations.

Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$\begin{aligned} K_c &= \frac{[\mathrm{PCl_3}]\,[\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = 0.0211 \\ &= \frac{(x)(x)}{(1.00 - x)} \\ 0.0211 &= \frac{(x)(x)}{(1.00 - x)} \\ 0.0211(1.00 - x) &= x^2 \\ x^2 + 0.0211x - 0.0211 &= 0 \end{aligned}$$

We can solve for x using the quadratic equation. An equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for *a*, *b*, and *c* yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$
$$= \frac{-0.0211 \pm \sqrt{\left(4.45 \times 10^{-4}\right) + \left(8.44 \times 10^{-2}\right)}}{2}$$
$$= \frac{-0.0211 \pm 0.291}{2}$$

The two roots of the quadratic are, therefore,

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

and

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

We will only use x = 0.135 M because the other solution results in a negative concentration which is not physically possible.

The equilibrium concentrations are

$$[\mathrm{PCl_5}] = 1.00 - 0.135 = 0.87 \text{ M}$$
$$[\mathrm{PCl_3}] = x = 0.135 \text{ M}$$
$$[\mathrm{Cl_2}] = x = 0.135 \text{ M}$$

Step 4.

Verify the calculated equilibrium concentrations, by substituting into the equilibrium expression:

$$K_c = \frac{[\mathrm{PCl_3}]\,[\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant computed using the equilibrium concentrations is close to the given K_c value, with minor differences due to rounding. This confirms that the calculation is accurate.

Exercise 7.4.4

A 1.00-L flask is filled with 1.00 mole of $\mathrm{H_2}$ and 2.00 moles of $\mathrm{I_2}$. What are the equilibrium concentrations of $\mathrm{H_2}$, $\mathrm{I_2}$, and HI?

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \quad K_c = 50.5$$

Answer available at the end of this section.

Simplifying Assumption (a.k.a. 'The Approximation')

In the previous examples, we solved for equilibrium concentrations with the quadratic formula. This method is always valid but time-consuming. Fortunately, a faster approach can often give similar answers. Our chemical intuition guides us to when an approximation might be effective. After solving with the shorter method, we can easily check our answer to ensure the concentrations we found are sufficiently accurate.

Consider the following reaction:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)} \quad K_c = 7.6 \times 10^{-4}$$

Since K_c is very small ($\ll 1$), this reaction favours the reactants (the denominator is much larger than the numerator in the K_c expression). This means that, at equilibrium, the mixture will mostly be $\mathrm{N_2O_4}$ with only small amounts of $\mathrm{NO_2}$ present.

Now consider a specific example where the initial concentration of N_2O_4 is 0.15 M, no products are present at the start, and we must determine the concentrations of each species at equilibrium to two significant figures. The ICE table is:

	$N_2O_4\,(g)$ ⇌	$2\,NO_2\,(g)$
Initial	0.15 M	0 M
Change	- x	+2x
Equilibrium	0.15 M - x	2x

Here is where our chemical intuition helps. Because K_c for this reaction is very small, the equilibrium mixture will be mostly reactants. In addition, we are starting with only N_2O_4. In other words, the initial conditions in this problem are already close to the equilibrium conditions. Therefore, the change in [N_2O_4] (the -x) will likely be small compared with the initial value (0.15 M).

Why does this matter? From the ICE table, the expression for the equilibrium concentration of N_2O_4 is $0.15–x$, which has two terms (a binomial). If x << 0.15, this approximation is likely to be valid:

(0.15–x) ≈ 0.15

At this point, are we certain this approximation will work? No. However, this assumption makes the calculation so much simpler that it's time-efficient to try it and then check afterwards.

The equilibrium expression is:

$$K_c = \frac{[NO_2{}^2]}{[N_2O_4]} = \frac{(2x)^2}{(0.15 - x)} = 7.6 \times 10^{-4}$$

With the approximation (0.15–x) ≈ 0.15, we can write:

$$K_c = \frac{(2x)^2}{(0.15)} = 7.6 \times 10^{-4}$$

This makes solving for x much simpler than using the quadratic equation:

$$\frac{4x^2}{(0.15)} = 7.6 \times 10^{-4} \quad x = 0.0053$$

Before moving on, check whether the assumption was reasonable. We assumed that x was 'small' relative to 0.15 M. Was it?

$$\frac{(0.0053)}{0.15} \times 100\% = 3.6\%$$

The change is fairly small, only 3.6% of the initial concentration. In general, whether this precision is 'sufficient' depends on the situation - perhaps good enough for mixing a quick solution, but not for high-accuracy analytical techniques.

In CHM 135, we use this rule for equilibrium approximations: If the neglected term is less than 5% of the other term in the binomial, the approximation is valid. Here, since 3.6% < 5%, using the simplifying assumption is justified.

To complete the problem, we'd use the value of x that we found to determine the concentrations at equilibrium:

[\ce{N2O4}\)]=0.15–(0.0053)=0.1447 M = 0.14 M (two significant figures)

[NO_2]=2x=2(0.0053)=0.011 M

In CHM 135, if an assumption is made in an equilibrium calculation, it must be explicitly stated and justified by checking against the initial quantity. The 5% rule provides a useful guideline for determining whether an approximation is reasonable. If the

assumption is not valid, a more precise method (such as the quadratic formula) should be used.

Example 7.4.5: Calculation of Equilibrium Concentrations

The decomposition of phosgene occurs via the following reaction:

$$\mathrm{COCl_2\,(g)} \rightleftharpoons \mathrm{CO\,(g) + Cl_2\,(g)} \qquad K_p = 3.4 \times 10^{-10} \text{ at } 375 \text{ K}$$

If a sealed vessel containing 3.5 atm of $\mathrm{COCl_2}$ comes to equilibrium, what are the partial pressures of all of the species?

Solution

	$\mathrm{COCl_2\,(g)}$ ⇌	$\mathrm{CO\,(g)}$ +	$\mathrm{Cl_2\,(g)}$
Initial	3.5 atm	0 atm	0 atm
Change	- x	+x	+x
Equilibrium	3.5 atm - x	x	x

Substitute the equilibrium pressure terms into the K_p expression

$$K_p = \frac{P_{CO}P_{Cl_2}}{P_{COCl_2}} = \frac{(x)(x)}{3.5-x} = 3.4 \times 10^{-10}$$

Since K_p is very small, we can assume that the change in pressure of $\mathrm{COCl_2}$ is negligible compared to the initial pressure. Thus, we can approximate (3.5–x) ≈ 3.5, because x is much smaller than the initial pressure.

$\frac{x^2}{3.5} = 3.4 \times 10^{-10}$ $x = 3.4 \times 10^{-5}\mathrm{atm}$
Let's check the validity of our assumption:

$\frac{3.4\times10^{-5}}{3.5}x100\% = 0.001\%$,

which is much smaller than 5%, confirming the assumption is valid.

The equilibrium pressures are $P_{COCl_2} = 3.5 \text{ atm}, P_{CO} = P_{Cl_2} = 3.4 \times 10^{-5}\mathrm{atm}$.

Checking our calculation gives:
$K_p = \frac{P_{CO}P_{Cl_2}}{P_{COCl_2}} = \frac{(3.4\times10^{-5})(3.4\times10^{-5})}{3.5} = 3.3 \times 10^{-10}$. This value is very close to the K_p value.

Exercise 7.4.5

At 700 K, $K_c = 4.25 \times 10^{-9}$ for the reaction:

$$2\,\mathrm{HBr\,(g)} \rightleftharpoons \mathrm{H_2\,(g) + Br_2\,(g)}$$

0.018 M of HBr gas is placed in a sealed flask. What are the equilibrium concentrations of all of the species?

Answer available at the end of this section.

Summary

In equilibrium problems, we use concentrations or pressures to calculate the equilibrium constant, K_c or K_p, or use equilibrium constants to determine equilibrium concentrations or pressures. The changes in concentration (or pressure) as the system moves toward equilibrium are proportional to the stoichiometric coefficients in the balanced chemical equation. The sign of the change is positive when the concentration (or pressure) increases and negative when it decreases.

ICE (Initial, Change, Equilibrium) tables provide a structured way to organize information for equilibrium problems. The stoichiometric coefficients of the balanced equation determine the relative changes in the reactant and product concentrations.

To simplify calculations, when K is very small, we can assume that the change in concentration or pressure is negligible compared to the initial value. This assumption is valid when the change is less than 5% of the initial concentration (or pressure). If the assumption cannot be made, a more detailed calculation often involving the quadratic equation may be necessary.

Glossary

5% rule
: When calculating equilibrium concentrations, if the change in concentration is less than 5% of the initial concentrations, then the change can be mathematically disregarded.

ICE table
: A method of calculating equilibrium concentration by tracking how a system moves from its initial concentration (I) through the changes (C) to equilibrium (E)

Answers

Exercise 7.4.1

(a) 2*x*, *x*, −2*x*; (b) *x*, −2*x*; (c) −4*x*, −7*x*, 4*x*, 6*x*

Exercise 7.4.2

	$PCl_3(g)$ +	$Cl_2(g)$ ⇌	$PCl_5(g)$
Initial	0.480 atm	0.400 atm	0 atm
Change	- x	-x	+x
Equilibrium	0.480 - x	0.400 - x	x = 0.320

$P_{PCl_3} = 0.480 - 0.320 = 0.160 \text{ atm}$
$P_{Cl_2} = 0.400 - 0.320 = 0.080 \text{ atm}$
$P_{PCl_5} = 0.320 \text{ atm}$
$K_p = \frac{P_{PCl_5}}{P_{PCl_3}P_{Cl_2}} = \frac{0.320}{(0.160)(0.080)} = 25$

Exercise 7.4.3

$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = 6.00 \times 10^{-2}$
$[NH_3] = \sqrt{\frac{[N_2][H_2]^3}{K_c}} = \sqrt{\frac{(4.26)(2.09)^3}{6.00\times10^{-2}}} = 25.5M$

Exercise 7.4.4

	$H_2(g)$ +	$I_2(g)$ ⇌	$2\,HI(g)$
Initial	1.00 M	2.00 M	0 M
Change	- x	-x	+2x
Equilibrium	1.00 M- x	2.00 - x	2x

$K_c = \frac{[HI]^2}{[I_2][H_2]} = \frac{(2x)^2}{(1.00-x)(2.00-x)} = 50.5$
$4x^2 = 50.5(2.00 - 3.00x + x^2)$
$0 = 46.5x^2 - 151.5x + 101$
Using quadratic equation we get x = 2.32 M and 0.935 M. 2.32 M would give negative concentrations, so only 0.934 M is physically reasonable.
[H_2]=1.00 M - 0.935 M = 0.065 M
[I_2] = 2.00 M - 0.935 M = 1.065 M
[HI] = 2(0.935 M) = 1.87 M
Double-checking:
$K_c = \frac{[HI]^2}{[I_2][H_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 50.5$

Exercise 7.4.5

	$2\,HBr\,(g)$ ⇌	$H_2\,(g)$ +	$Br_2\,(g)$
Initial	0.018 M	0 M	0 M
Change	- 2x	+x	+x
Equilibrium	0.018M- 2x	x	x

$K_c = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{(x)(x)}{(0.018-2x)^2} = 4.25 \times 10^{-9}$

Since K_c is very small, we can assume that the change in concentration of HBr is negligible compared to the initial concentration. Thus, we can approximate (0.018–2x) ≈ 0.018, because x is much smaller than the initial concentration:

$\frac{(x)(x)}{(0.018)^2} = 4.25 \times 10^{-9}\ x^2 = 1.38 \times 10^{-12}\ x = 1.2 \times 10^{-6} M$

Let's check the validity of our assumption, the percentage change in [HBr] is

$\frac{1.2\times10^{-6}M}{0.018M} \times 100\% = 0.0065\%$,

which is much smaller than 5%, confirming the assumption is valid.

The equilibrium concentrations are [HBr] = 0.018 M, $[H_2]$ = $[Br_2]$ = 1.2 x 10^{-6} M.

Double-checking our calculation gives:

$\frac{(1.2\times10^{-6})(1.2\times10^{-6})}{(0.018)^2} = 4.4 \times 10^{-9}$ This value is very close to the K_c value.

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7.5: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

- Use Le Chatelier's principle to predict how changes in reaction conditions affect the equilibrium position, composition, and equilibrium constant (K).

A system at equilibrium is in a state of dynamic balance, with the forward and reverse reactions occurring at equal rates. When a change in conditions affects the rates of these reactions unequally, the system is no longer at equilibrium. In response, the system undergoes a net reaction to restore equilibrium.

This behaviour is described by Le Chatelier's Principle, which states:

> When a chemical system at equilibrium is disturbed, it will shift in the direction that counteracts the change and re-establishes equilibrium.

Effect of a Change in Concentration

If the concentration of a reactant or product changes, the system will respond to restore equilibrium by favouring either the forward or reverse reaction. A concentration change will cause a change in the rate of either the forward or the reverse reaction.

Consider the equilibrium reaction

$$\mathrm{H_2\,(g) + I_2\,(g)} \rightleftharpoons \mathrm{2\,HI\,(g)} \quad K_c = 50.0 \text{ at } 400^\circ C$$

The rate laws for the forward and reverse reactions are:

$$\begin{aligned} &\text{forward} \quad \mathrm{H_2\,(g) + I_2\,(g)} \rightarrow \mathrm{2\,HI\,(g)} && \text{rate}_f = k_f[\mathrm{H_2}]^m[\mathrm{I_2}^n] \\ &\text{reverse} \quad \mathrm{2\,HI\,(g)} \rightarrow \mathrm{H_2\,(g) + I_2\,(g)} && \text{rate}_r = k_r[\mathrm{HI}]^x \end{aligned}$$

At equilibrium:

$$\text{rate }_f = \text{ rate }_r$$

Adding reactant ($\mathrm{H_2}$ or $\mathrm{I_2}$) increases the rate of the forward reaction:

$$\text{rate}_f > \text{ rate }_r$$

As a result, the net reaction is in the forward direction (right), consuming reactants and producing HI. Removing a product HI results in the same shift as it decreases the rate of the reverse reaction, shifting the equilibrium right.

Conversely, removing a reactant or adding a product increases the rate of the reverse reaction, shifting the net reaction in the reverse direction (left) to restore equilibrium.

$$\text{rate }_f < \text{ rate }_r$$

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be understood in terms of reaction quotients. At equilibrium:

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}]\,[\mathrm{I_2}]} = K_c$$

If a reactant is added (increasing the denominator) or a product is removed (decreasing the numerator), then \(Q_c

If a reactant is removed or a product is added, then $Q_c > K_c$ and the net reaction is in the reverse direction to restore equilibrium

such that $Q_c = K_c$.

Despite these shifts, the value of K_c remains constant, but the equilibrium concentrations adjust accordingly.

For gas-phase equilibria, changes in partial pressure have the same effect as concentration changes because the P of an ideal gas is proportional to its molar concentration M:

$$M = \frac{n}{V} = \frac{P}{RT}$$

Thus, changing the partial pressures of any reactant or product alters its concentrations, resulting in the same effects on the equilibrium.

Effect of a Change in Volume

For a gas-phase reaction, changes in volume affect the partial pressures of all species, potentially shifting the equilibrium depending on the reaction's stoichiometry. Since all gases occupy the same volume, a decrease in volume increases the partial pressures (and concentrations) of all gases proportionally. To predict the direction of the shift, the total number of gas molecules on each side of the reaction must be considered.

At equilibrium, the reaction:

$$\mathrm{H_2\,(g) + I_2\,(g) \;\rightleftharpoons\; 2\,HI\,(g)}$$

is described by the reaction quotient:

$$Q_p = \frac{P_{\mathrm{HI}}^2}{P_{\mathrm{H_2}} P_{\mathrm{I_2}}} = K_p$$

If the volume decreases by a factor of 3, the partial pressures of all species increase by the same factor:

$$\begin{aligned} Q_p{}' &= \frac{(3P_{\mathrm{HI}})^2}{(3P_{\mathrm{H_2}})\,(3P_{\mathrm{I_2}})} = \frac{9\,P_{\mathrm{HI}}^2}{9\,P_{\mathrm{H_2}} P_{\mathrm{I_2}}} = \frac{P_{\mathrm{HI}}^2}{P_{\mathrm{H_2}} P_{\mathrm{I_2}}} \\ &= Q_p = K_p \end{aligned}$$

Since both sides have the same number of moles of gas, the reaction remains at equilibrium despite the volume change.

Now consider a different system, again decreasing the volume by a factor of three:

$$\mathrm{2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)}$$

At equilibrium:

$$Q_p = \frac{P_{\mathrm{NO}}^2\, P_{\mathrm{O_2}}}{P_{\mathrm{NO_2}}^2} = K_p$$

After the volume change, the partial pressures of all species increase by a factor of 3:

$$\begin{aligned} Q_p{}' &= \frac{(3P_{\mathrm{NO}})^2\,(3P_{\mathrm{O_2}})}{(3P_{\mathrm{NO_2}})^2} = \frac{9\,P_{\mathrm{NO}}^2 \cdot 3\,P_{\mathrm{O_2}}}{9\,P_{\mathrm{NO_2}}^2} = \frac{27\,P_{\mathrm{NO}}^2\,P_{\mathrm{O_2}}}{9\,P_{\mathrm{NO_2}}^2} \\ &= 3\,Q_p > K_p \end{aligned}$$

Since $Q_p^{'} > K_p$, the system shifts left (toward reactants) to reestablish equilibrium ($Q_p^{'} = K_p$), favouring the formation of $\mathrm{NO_2}$.

These examples illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume change. If the number of moles of gas on the reactant and product sides of the reaction are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, both the effect of the volume change and the number of moles of gas on the reactant and product side must be considered.

- If the volume decreases (increasing pressure and concentration), the reaction will shift to the side with fewer moles of gas.
- If the volume increases (decreasing pressure and concentration), the reaction will shift to the side with more moles of gas.

The issue of volume is not isolated to gasses as volumes can change in solutions by adding or removing the solvent. Rule defined above also applies to solutions:

- If the volume decreases (e.g. solvent removed) all concentrations will increase and the reaction will shift to the side with fewer solution phase moles (e.g. aqueous).
- If the volume increases (e.g. solvent added) all concentrations will decrease and the reaction will shift to the side with more solution phase moles.

Chemistry in Everyday Life: Equilibrium and Soft Drinks

The refreshing fizz in carbonated soft drinks traces back to a groundbreaking discovery in 1767. English chemist Joseph Priestley was the first to create "carbonated" water by dissolving carbon dioxide gas ($\mathrm{CO_2}$) in water. He produced the gas by reacting sulfuric acid with calcium carbonate and then infused it into water, laying the foundation for the fizzy beverages we enjoy today.

The fizz is the result of a series of equilibrium reactions:

$$\begin{aligned}
&\text{dissolution} && \mathrm{CO_2\,(g) \rightleftharpoons CO_2\,(aq)}\\
&\text{hydrolysis} && \mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}\\
&\text{ionization} && \mathrm{H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons HCO_3{}^-\,(aq) + H_3O^+\,(aq)}
\end{aligned}$$

Modern carbonated drinks are produced under high pressure, which shifts the dissolution equilibrium to the right, allowing for a high concentration of dissolved $\mathrm{CO_2}$.

When a bottle or can is opened, the pressurized $\mathrm{CO_2}$ escapes with a characteristic hiss, shifting the dissolution equilibrium left as $\mathrm{CO_2\,(g)}$ is released. This also causes the hydrolysis and ionization equilibria to shift left, reducing the concentrations of hydrogen carbonate $\mathrm{HCO_3{}^-}$ and hydronium ions $\mathrm{H_3O^+}$. Over time, the beverage loses its fizz and becomes slightly less acidic, though the change in acidity is less noticeable than the lack of carbonation.

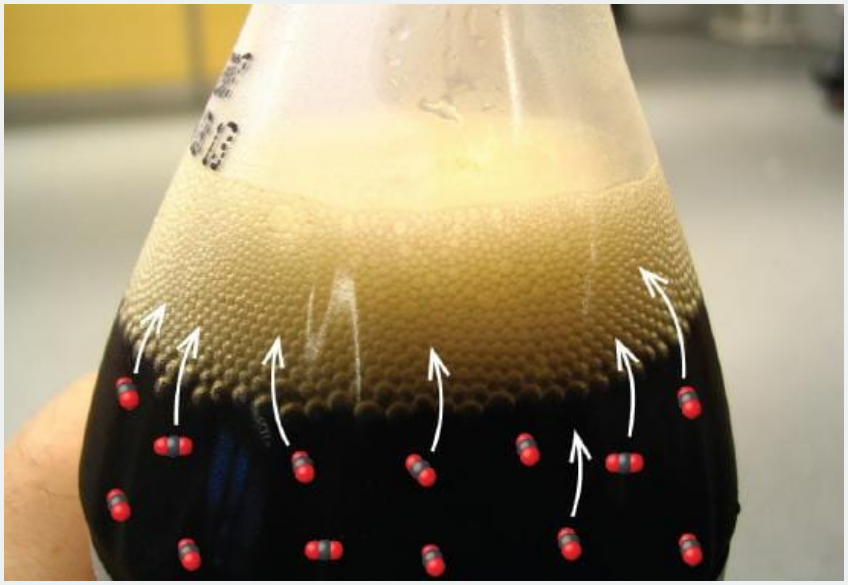


Figure 7.5.1: Opening a soft-drink bottle lowers the $\mathrm{CO_2}$ pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved $\mathrm{CO_2}$ from the beverage. (credit: modification of work by “D Coetzee”/Flickr)

Effect of a Change in Temperature

When an equilibrium is stressed by a change in concentration or volume, the system will shift to re-establish equilibrium, but the

equilibrium constant (K) remains unchanged. However, when a change in temperature stresses an equilibrium, the system shifts to a new equilibrium position with a different relative composition and a different value of K.

Consider the elementary reaction:

$$A \rightleftharpoons B$$

Since this is an elementary reaction, the rate laws for the forward and reverse can be derived directly from the balanced equation's stoichiometry:

$$\text{rate}_f = k_f[A]$$
$$\text{rate}_r = k_r[B]$$

At equilibrium:

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives:

$$k_f[A] = k_r[B]$$
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

Thus, the equilibrium constant (K_c) is the ratio of the rate constants for the forward and reverse reactions. Since the rate constants (k_f and k_r) depend on temperature (as described by the Arrhenius equation), the equilibrium constant (K) also varies with temperature. The extent of this variation depends on how temperature affects both rate constants. For complex reactions involving multiple steps, a similar but more intricate relationship exists between K and the rate constants for individual steps. Regardless of complexity, the equilibrium constant will always be temperature-dependent.

The direction of the equilibrium shift in response to temperature changes depends on whether the reaction is exothermic or endothermic:

- Increasing temperature shifts equilibrium in the endothermic direction, absorbing heat.
- Decreasing temperature shifts equilibrium in the exothermic direction, releasing heat.

For example, the decomposition of dinitrogen tetroxide is an endothermic process:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)} \quad \Delta H = +57.20\ \mathrm{kJ}$$

For the purposes of Le Chatelier's principle, heat can be treated as a reactant in an endothermic reaction:

$$\text{heat} + \mathrm{N_2O_4\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)}$$

- Increasing temperature adds heat, shifting the equilibrium right (toward products) in the endothermic direction, because of an increase in the value of K.
- Decreasing temperature removes heat, shifting the equilibrium left (toward reactants) in the exothermic direction, because of a decrease in the value of K.

For exothermic reactions, heat can be considered a product, leading to opposite temperature dependence:

$$\mathrm{R} \rightleftharpoons \mathrm{P} + \text{heat}$$

- Increasing temperature shifts equilibrium left (toward reactants), decreasing the value of K.
- Decreasing temperature shifts equilibrium right (toward products), increasing the value of K.

Effect of a Catalyst

A catalyst is a substance that speeds up a reaction by providing an alternative reaction pathway with a lower activation energy. A catalyst lowers the activation energy for both the forward and reverse reactions, allowing the system to reach equilibrium more quickly. However, a catalyst does not affect the equilibrium position or the equilibrium constant (K). The catalyst only reduces the

time required to reach equilibrium—it does not change the equilibrium concentrations of reactants or products.

Example 7.5.1

Consider the following reaction:

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)}$$

How will the following changes affect the equilibrium concentration of [HI]? Will the changes affect the equilibrium constant, K?

a. Increasing [$\mathrm{I_2}$]

b. Decreasing [HI]

c. Doubling volume

d. Increasing temperature

Solution

$$Q_c = \frac{[HI]^2}{[H_2][I_2]}$$

a. When $\mathrm{I_2}$ is added, the denominator of Q_c increases, so $Q_c < K_c$. The reaction proceeds towards products (to the right) until equilibrium is re-established, so [HI] increases. K_c does not change.

b. When $\mathrm{H_2}$ is removed, the denominator of Q_c decreases, so $Q_c > K_c$. The reaction proceeds towards reactants (to the left) until equilibrium is re-established, so [HI] decreases. K_c does not change.

c. For this reaction, the number of moles of gas is the same on the reactant and product side, so the volume will have no effect of the [HI]. K_c does not change.

d. Since the reaction is exothermic, we can consider heat a product:

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)}$$

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} + heat$$

Adding heat (increasing temperature) shifts the reaction to the left, towards reactants. This will decrease [HI]. K_c will also decrease.

Application of Equilibrium Concepts: The Haber-Bosch Process

A real-world example of equilibrium principles in action is the industrial production of ammonia ($\mathrm{NH_3}$). Ammonia ranks among the top 10 industrial chemicals by production volume, with Canada producing approximately 5 million tonnes annually. This compound is a key ingredient in manufacturing fertilizers, plastics, dyes, and explosives, making it vital to modern industry.

Most industrial ammonia is synthesized via the Haber-Bosch process, which relies on the following equilibrium reaction:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \quad \Delta H = -92.2\ \mathrm{kJ}$$

The characteristics of this reaction present challenges for efficient production. The equilibrium constant (K_p) is relatively small (on the order of 10^{-5} at 25 °C), meaning that only a small amount of ammonia is present in an equilibrium mixture at standard conditions. Additionally, the reaction proceeds slowly at low temperatures.

To maximize ammonia production, the Haber-Bosch process is designed to exploit equilibrium principles and overcome these challenges:

- High pressures: Reactants are subjected to pressures of approximately 150–250 atm, shifting the equilibrium right and favouring ammonia formation.
- Continuous removal of ammonia: Ammonia is collected as it forms, reducing its concentration in the mixture and shifting the equilibrium right.
- Moderate temperatures with a catalyst: While low temperatures favour product formation for this exothermic reaction, they result in an inefficiently slow reaction rate. To balance yield and rate, the process operates at moderate temperatures (400–500 °C) with a catalyst to accelerate the reaction.

A diagram illustrating a typical industrial setup for the Haber-Bosch process is shown in Figure 7.5.2:

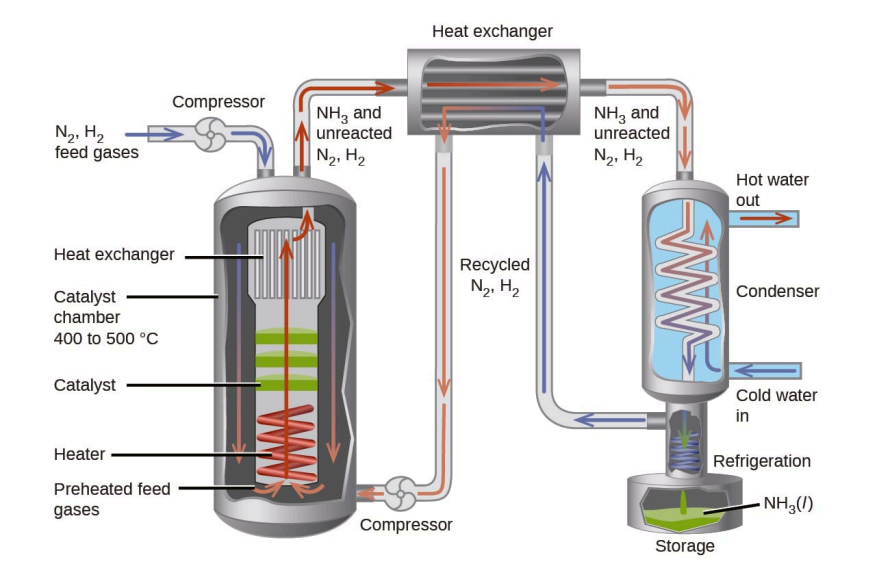


Figure 7.5.2: The figure shows a typical industrial setup for the commercial production of ammonia by the Haber-Bosch process. The process operates under conditions that stress the chemical equilibrium to favour product formation.

Summary

Le Chatelier's Principle describes how a system at equilibrium responds to a disturbance: the system undergoes a net reaction to reduce the disturbance and re-establishes equilibrium.

- Changes in concentration: Adding a reactant or product causes a net reaction to consume the added component, removing a reactant or product causes a net reaction to produce the affected species. The equilibrium constant (K) remains unchanged.
- Changes in volume (for gas-phase equilibria): Decreasing the volume (increasing pressure) shifts the equilibrium toward the side with fewer gas molecules, while increasing the volume (decreasing pressure) shifts it toward the side with more gas molecules. When the number of gas molecules is equal on both sides, volume changes do not affect equilibrium. The equilibrium constant (K) remains unchanged. Similar changes in response to volume can be relevant to solution-based reactions and changes in solvent.
- Changes in temperature: Increasing temperature shifts equilibrium in the endothermic direction (absorbing heat), while decreasing temperature shifts it in the exothermic direction (releasing heat). Unlike concentration or volume changes, temperature changes alter both the equilibrium position and the value of K.
- Catalysts: Catalysts accelerate the rate at which equilibrium is reached by lowering the activation energy for both the forward and reverse reactions. However, they do not change the equilibrium position or the value of K.

Glossary

La Chatelier's principle

When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

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7.E: Equilibrium Fundamentals (Exercises)

Chemical Equilibrium

Exercise 7.E.1*

When can a reversible reaction be considered to be at equilibrium?

Answer available at the end of this section.

Exercise 7.E.2*

If the concentrations of products and reactants are equal, can the system be considered at equilibrium?

Answer available at the end of this section.

Reaction Quotients and Equilibrium Constants

Exercise 7.E.3*

Write the expression for the reaction quotient, Q_c, for each of the following reactions:

a. $\mathrm{CH_4}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{CH_3Cl}(g) + \mathrm{HCl}(g)$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g)$
c. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
d. $\mathrm{BaSO_3}(s) \rightleftharpoons \mathrm{BaO}(s) + \mathrm{SO_2}(g)$
e. $\mathrm{P_4}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{P_4O_{10}}(s)$
f. $\mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{Br}(g)$
g. $\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$
h. $\mathrm{CuSO_4 \cdot 5\,H_2O}(s) \rightleftharpoons \mathrm{CuSO_4}(s) + 5\,\mathrm{H_2O}(g)$

Answer available at the end of this section.

Exercise 7.E.4*

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$ $K_c = 17$; $[\mathrm{NH_3}]$ = 0.20 M, $[\mathrm{N_2}]$ = 1.00 M, $[\mathrm{H_2}]$ = 1.00 M
b. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$ $K_p = 6.8 \times 10^4$; initial pressures: $\mathrm{NH_3}$ = 3.0 atm, $\mathrm{N_2}$ = 2.0 atm, $\mathrm{H_2}$ = 1.0 atm
c. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ $K_c = 0.230$; $[\mathrm{SO_3}]$ = 0.00 M, $[\mathrm{SO_2}]$ = 1.00 M, $[\mathrm{O_2}]$ = 1.00 M
d. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ $K_p = 16.5$; initial pressures: $\mathrm{SO_3}$ = 1.00 atm, $\mathrm{SO_2}$ = 1.00 atm, $\mathrm{O_2}$ = 1.00 atm
e. $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g)$ $K_c = 4.6 \times 10^4$; $[\mathrm{NO}]$ = 1.00 M, $[\mathrm{Cl_2}]$ = 1.00 M, $[\mathrm{NOCl}]$ = 0 M
f. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g)$ $K_p = 0.050$; initial pressures: NO = 10.0 atm, $\mathrm{N_2}$ = $\mathrm{O_2}$ = 5 atm

Answer available at the end of this section.

Exercise 7.E.5*

The equilibrium constant, K_p, for the reaction, $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ is 16.5. What is the value of K_p for each of the following reactions at the same temperature?

a. $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}\,O_2(g)$
b. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
c. $SO_2(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons SO_3(g)$

Answer available at the end of this section.

Exercise 7.E.6*

Calculate the value of the equilibrium constant, K_c, at 298 K for the following reaction:

$$A_2\,(g) + 2\,B_2\,(g) \rightleftharpoons 2\,AB_2\,(g)$$

from the following K_c values at 298 K.

$$A_2\,(g) + B_2\,(g) \rightleftharpoons 2\,AB\,(g) \quad K_c = 12$$

$$2\,AB_2\,(g) \rightleftharpoons 2\,AB\,(g) + B_2\,(g) \quad K_c = 0.25$$

Answer available at the end of this section.

Exercise 7.E.7*

Convert the values of K_c to values of K_p or the values of K_p to values of K_c.

a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.50 \text{ at } 400°C$
b. $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad K_c = 50.2 \text{ at } 448°C$
c. $Na_2SO_4 \cdot 10\,H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10\,H_2O(g) \quad K_p = 4.08 \times 10^{-25} \text{ at } 25°C$
d. $H_2O(l) \rightleftharpoons H_2O(g) \quad K_p = 0.122 \text{ at } 50°C$

Answer available at the end of this section.

Equilibrium Calculations

Exercise 7.E.8*

An equilibrium mixture of $NH_3\,(g)$, $H_2\,(g)$, and $N_2\,(g)$ at 500 °C was found to contain 1.35 M H_2, 1.15 M N_2, and 4.12×10^{-1} M NH_3.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

What is the value of the K_c at 500 °C?

Answer available at the end of this section.

Exercise 7.E.9*

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \rightleftharpoons 3\,\mathrm{H_2}(g) + \mathrm{CO}(g)$$

What is the equilibrium constant, K_p, for the reaction if a mixture at equilibrium contains gases with the following pressures: $\mathrm{CH_4}$, 10.7 atm; $\mathrm{H_2O}$, 20.5 atm; CO, 10.7 atm; $\mathrm{H_2}$, 97.5 atm; at a temperature of 760 °C?

Answer available at the end of this section.

Exercise 7.E.10**

A 0.72-mol sample of $\mathrm{PCl_5}$ is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $\mathrm{PCl_3\,(g)}$ and 0.40 mol of $\mathrm{Cl_2\,(g)}$. Calculate K_c for the decomposition of $\mathrm{PCl_5}$ to $\mathrm{PCl_3}$ and $\mathrm{Cl_2}$ at this temperature.

$$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g)$$

Answer available at the end of this section.

Exercise 7.E.11*

Analysis of the gases in a sealed reaction vessel containing $\mathrm{NH_3}$, $\mathrm{N_2}$, and $\mathrm{H_2}$ at equilibrium at 400 °C established the concentration of $\mathrm{N_2}$ to be 1.2 M and the concentration of $\mathrm{H_2}$ to be 0.24 M.

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \quad K_c = 0.50 \text{ at } 400\ ^\circ\mathrm{C}$$

Calculate the equilibrium molar concentration of $\mathrm{NH_3}$.

Answer available at the end of this section.

Exercise 7.E.12*

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$\mathrm{CoO}(s) + \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) + \mathrm{CO_2}(g) \quad K_c = 4.90 \times 10^2 \text{ at } 550\ ^\circ\mathrm{C}$$

What concentration of CO remains in an equilibrium mixture with [$\mathrm{CO_2}$] = 0.100 M?

Answer available at the end of this section.

Exercise 7.E.13**

What are the concentrations of $\mathrm{H_2O}$, $\mathrm{Cl_2O}$, and HOCl in an equilibrium mixture produced by the reaction below when 2.00 mol of $\mathrm{H_2O\,(g)}$ is added to 2.00 mol of $\mathrm{Cl_2O\,(g)}$ in a 2.00 L flask?

$$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\,\mathrm{HOCl}(g) \quad K_c = 0.180$$

Answer available at the end of this section.

Exercise 7.E.14**

Calculate the equilibrium concentrations of N_2O_4 and NO_2 in a 1.00 L vessel in the gas mixture that was prepared from 0.129 mol of N_2O_4.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 1.07 \times 10^{-5}$$

Answer available at the end of this section.

Exercise 7.E.15**

0.129 mol of $\mathrm{IBr\,(g)}$ is added to a 1.00 L flask. What are the concentrations of I_2, Br_2 and IBr when equilibrium is reached?

$$I_2(g) + Br_2(g) \rightleftharpoons 2\,IBr(g) \quad K_c = 280.0$$

Answer available at the end of this section.

Le Chatelier's Principle

Exercise 7.E.16*

Predict the effect of increasing the container volume on the equilibrium amounts of reactants and products in the following reactions:

a. $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

b. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$

c. $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$

d. $Br_2(g) \rightleftharpoons 2\,Br(g)$

Answer available at the end of this section.

Exercise 7.E.17*

How would you adjust the volume of the container in order to maximize the product yield in these reactions?

a. $CuSO_4 \cdot 5\,H_2O(s) \rightleftharpoons CuSO_4(s) + 5\,H_2O(g)$

b. $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

Answer available at the end of this section.

Exercise 7.E.18*

How will an increase in temperature affect each of the following equilibria?

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad \Delta H = 92\ \mathrm{kJ}$
b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\ \mathrm{kJ}$
c. $2\,O_3(g) \rightleftharpoons 3\,O_2(g) \quad \Delta H = -285\ \mathrm{kJ}$
d. $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \quad \Delta H = -176\ \mathrm{kJ}$

Answer available at the end of this section.

Exercise 7.E.19**

Suggest four ways in which the equilibrium concentration of hydrazine, N_2H_4, could be increased :

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \quad \Delta H = 95 \text{ kJ}$$

Answer available at the end of this section.

Exercise 7.E.20**

The following reaction is used in removing the pollutant sulfur dioxide from factory gases:

$\mathrm{CaO\,(s) + SO_2\,(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons CaSO_4\,(s)}$

How does the equilibrium position shift as a result of the following changes? Do these changes affect the value of K_c?

a. Doubling the amount of $\mathrm{CaO\,(s)}$

b. Removing half of the $\mathrm{CaSO_4\,(s)}$

c. Removing half of the $\mathrm{SO_2\,(g)}$

d. Doubling the pressure of $\mathrm{O_2\,(g)}$

e. Increasing the volume of the reaction container

Answer available at the end of this section.

Additional Problems

Exercise 7.E.21**

At 723 K, $K_p = 6.5 \times 10^{-6}$ for the reaction $\mathrm{2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)}$ An empty container is filled with NO_2 gas to a pressure of 1.5 atm. What are the equilibrium pressures of all of the gases?

Answer available at the end of this section.

Exercise 7.E.22**

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:

$$2\,H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90.2\,\text{kJ}$$

a. What is the expression for the equilibrium constant (K_c)?
b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
c. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?
d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?
e. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

f. What will happen to the concentrations of $\mathrm{H_2}$, CO, and $\mathrm{CH_3OH}$ at equilibrium if more catalyst is added?

Answer available at the end of this section.

Exercise $7.E.23$***

Consider the reaction $A(g) \rightleftharpoons B(g)$. At 298 K, an equilibrium mixture is analyzed and found to contain [A] = 0.80 M and [B] = 2.4 M.

a. Additional B(g) is added to give [B] = 3.2 M, without changing the [A]. Which direction will the reaction shift to re-establish equilibrium?

b. What are the new concentrations of [A] and [B] when equilibrium is re-established?

c. The temperature of the mixture is then increased to 350 K. After equilibrium is again re-established, [A] = 0.70 M and [B] = 3.3 M. What is K_c at 350 K? What does this indicate about the reaction?

Answer available at the end of this section.

Exercise $7.E.24$***

At 355 K, a 10.0 L flask contains $\mathrm{BaO\,(s)}$, $\mathrm{BaSO_3\,(s)}$, and $\mathrm{SO_2\,(g)}$ at equilibrium with a partial pressure of $\mathrm{SO_2}$ of 9.65 atm:

$$\mathrm{BaSO_3}(s) \rightleftharpoons \mathrm{BaO}(s) + \mathrm{SO_2}(g)$$

Without changing the amount of the solid $\mathrm{BaSO_3}$ or BaO present, the pressure of $\mathrm{SO_2}$ is increased to 9.89 atm. After equilibrium is re-established, what is the change in the mass of $\mathrm{BaO\,(s)}$ present?

Answer available at the end of this section.

Answers

Exercise $7.E.1$*

A reversible reaction is at equilibrium when the concentrations of reactants and products remain constant over time. Although both the forward and reverse reactions continue to occur, they do so at the same rate, resulting in no net change in the system.

Exercise $7.E.2$*

Equilibrium does not mean that the concentrations of products and reactants are equal. The composition of the reaction mixture at equilibrium depends on the value of the equilibrium constant, K. A large K value typically means the mixture contains mostly products, while a small K value indicates a mixture dominated by reactants. Therefore, while equal concentrations of reactants and products can occur at equilibrium in some cases, it is not a general condition for equilibrium.

Exercise $7.E.3$*

a. $Q_c = \dfrac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$

b. $Q_c = \dfrac{[NO]^2}{[N_2][O_2]}$

c. $Q_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

d. $Q_c = [\mathrm{SO_2}]$

e. $Q_c = \dfrac{1}{[P_4][O_2]^5}$

f. $Q_c = \dfrac{[Br]^2}{[Br_2]}$

g. $Q_c = \dfrac{[CO_2]}{[CH_4][O_2]^2}$

h. $Q_c = [\mathrm{H_2O}]^5$

Exercise $7.E.4$*

a. $Q_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{(1.00)(1.00)^3}{0.20^2} = 25$; $Q_c > K_c$, reaction proceeds left, towards reactants.

b. $Q_p = \frac{P_{N_2}P_{H_2}^3}{P_{NH_3}^2} = \frac{(2.0)(1.0)^3}{3.0^2} = 0.22$; $Q_p < K_p$, reaction proceeds right, towards products.

c. $Q_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(1.00)^2(1.00)}{0.00^2} = \infty$; $Q_c > K_c$, reaction proceeds left, towards reactants.

d. $Q_p = \frac{P^2_{SO_2}P_{O_2}}{P^2_{SO_3}} = \frac{(1.00)^2(1.00)}{1.00^2} = 1.00$; $Q_p < K_p$, reaction proceeds right, towards products.

e. $Q_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]} = \frac{0}{(1.00)^2(1.00)} = 0$; $Q_c < K_c$, reaction proceeds right, towards products.

f. $Q_p = \frac{P^2_{NO}}{P_{N_2}P_{O_2}} = \frac{10.0^2}{(5)(5)} = 4$; $Q_p > K_p$, reaction proceeds left, towards reactants.

Exercise $7.E.5$**

The expression for the equilibrium constant Kp for the original reaction is $K_p = \frac{P^2_{SO_2}P_{O_2}}{P^2_{SO_3}}$.

a. In this reaction, the coefficients of all species are halved relative to the original equation. When the coefficients are halved, the equilibrium constant is affected by the change in stoichiometry. Specifically, for each reactant or product whose coefficient is halved, we take the square root of its concentration term in the equilibrium expression.

The new equilibrium expression is $K_p{}' = \frac{P_{SO_2}P^{1/2}_{O_2}}{P_{SO_3}}$

Comparing this expression to the original, we see that each concentration term is raised to the 1/2 power. To find the value of K_p, we can take the square root.
$K_p{}' = \sqrt{K_p} = \sqrt{16.5} = 4.06$

b. In this reaction, the equation is reversed relative to the original. When a reaction is reversed, the equilibrium constant is the reciprocal of the original K_p. The equilibrium expression for this reversed reaction is

$K_p' = \frac{P^2_{SO_3}}{P^2_{SO_2}P_{O_2}} = \frac{1}{K_p} = \frac{1}{16.5} = 0.0606$

c. This reaction is the reverse of part (a), with the coefficients halved. The equilibrium expression for this reaction is
$K_p'' = \frac{P_{SO_3}}{P_{SO_2}P^{1/2}_{O_2}} = \frac{1}{K_p'} = 0.246.$

Exercise $7.E.6$**

$$\begin{aligned} \mathrm{A_2\,(g) + B_2\,(g) \rightleftharpoons \cancel{2\,AB(g)}} \qquad & K_c = 12 \\ \mathrm{\cancel{2\,AB(g)} + B_2\,(g) \rightleftharpoons 2\,AB_2\,(g)} \qquad & K_c' = \frac{1}{0.25} = 4.0 \\ \mathrm{A_2\,(g) + 2\,B_2\,(g) \rightleftharpoons 2\,AB_2\,(g)} \qquad & K = 12 \times 4.0 = 48 \end{aligned}$$

To find the equilibrium constant, we multiply the K_c values for the summed reactions:

$K_c = (12)(4.0) = 48$

Exercise $7.E.7$**

The relationship between K_c and K_p is $K_p = K_c(RT)^{\Delta n}$, where Δn is a change in the number of moles of gas from reactants to products.

a. $K_p = (0.50)(0.08206 \times 673)^{2-4} = 1.6 \times 10^{-4}$

b. $K_p = (50.2)(0.08206 \times 721)^0 = 50.2$ Since there is no change in the number of moles of gas, $K_c = K_p$.

c. $K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{4.08\times10^{-25}}{(0.08206\times298)^{10}} = 5.34 \times 10^{-39}$

d. $K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.122}{(0.08206\times323)^1} = 4.60 \times 10^{-3}$

Exercise $7.E.8$**

$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(4.12\times10^{-1})^2}{(1.15)(1.35)^3} = 0.0600$

Exercise $7.E.9$**

$K_p = \frac{P^3_{H_2}P_{CO}}{P_{CH_4}P_{H_2O}} = \frac{(97.5)^3(10.7)}{(10.7)(20.5)} = 4.52 \times 10^4$

Exercise $7.E.10$**

	$\mathrm{PCl_5\,(g)}$ ⇌	$\mathrm{PCl_3\,(g)}$ +	$\mathrm{Cl_2\,(g)}$
Initial	0.72 mol/L	0	0
Change	- x	+x	+x
Equilibrium	0.72 - x	x = 0.40 mol/L	x = 0.40 mol/L

We can calculate the molarities by dividing the number of moles by 1.00 L

$[\mathrm{PCl_5}]$ = 0.72 M - 0.40 M = 0.32 M

$K_c = \frac{[PCl_3][Cl_2]}{[PCl_3]} = \frac{(0.40)(0.40)}{(0.32)} = 0.50$

Exercise $7.E.11$*

$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}\ [NH_3] = \sqrt{K_c[N_2][H_2]^3} = \sqrt{(0.50)(1.2)(0.24)^3} = 0.091\ M$

Exercise $7.E.12$*

$K_c = \frac{[CO_2]}{[CO]}\ [CO] = \frac{[CO_2]}{K_c} = \frac{0.100}{4.90\times10^2} = 2.04 \times 10^{-4}\ M$

Exercise $7.E.13$**

The initial concentration can be calculated as follows: $\frac{2.00\ mol}{2.00\ L} = 1.00\ M$

	$\mathrm{H_2O\,(g)}$ +	$\mathrm{Cl_2O\,(g)}$ ⇌	$\mathrm{2\,HOCl\,(g)}$
Initial	1.00 M	1.00 M	0 M
Change	-x	- x	+2x

Equilibrium	1.00-x	1.00 - x	2x

$K_c = \frac{[HOCl_2]^2}{[H_2O][Cl_2O]} = \frac{(2x)^2}{(1.00-x)(1.00-x)} = 0.180$

Taking the square root of both sides, we get:

$\frac{2x}{1.00-x} = 0.424\ x = 0.175\ M$

$[H_2O]$ = $[Cl_2O]$ = 1.00 - x = 0.825 *M*; [HOCl] = 2x = 0.350 *M*.

(Alternatively, the expression can be expanded and the quadratic equation used to solve for x.)

Exercise $7.E.14$**

The initial $[N_2O_4] = \frac{0.129\ mol}{1.00\ L} = 0.129\ M$

	$N_2O_4(g)$ ⇌	$2\,NO_2(g)$
Initial	0.129 M	0 M
Change	- x	+2x
Equilibrium	0.129 - x	2x

$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.129-x)} = 1.07 \times 10^{-5}$

Assume x << 0.129 *M*:

$\frac{(2x)^2}{(0.129-x)} = \frac{(2x)^2}{(0.129)} = 1.07 \times 10^{-5}\ 4x^2 = 1.38 \times 10^{-6}\ x = 5.87 \times 10^{-4}\ M$

Let's check the validity of our assumption:

$\frac{5.87 \times 10^{-4}\ M}{0.129\ M} \times 100\% = 0.455\%$,

which is much smaller than 5%, confirming the assumption is valid.

$[NO_2]$ = 1.17 x 10^{-3} *M*

$[N_2O_4]$ = 0.128 *M*

Video solution

Exercise $7.E.15$**

The initial $[IBr] = \frac{0.129\ mol}{1.00\ L} = 0.129\ M$

The reaction proceeds from IBr to I_2 and Br_2, so the concentration will change accordingly:

	$I_2(g)$ +	$Br_2(g)$ ⇌	$2\,IBr(g)$
Initial	0 M	0 M	0.129 M
Change	+x	+x	-2x
Equilibrium	x	x	0.129 - 2x

$K_c = \frac{[IBr]^2}{[I_2][Br_2]} = \frac{(0.129-2x)^2}{x^2} = 280.0$

There are two approaches at this point. The expression can be expanded, and the quadratic equation can be used to find x. Alternatively, we can take the square root of both sides of the equation:

$\sqrt{\frac{(0.129-2x)^2}{x^2}} = \sqrt{280.0} = \frac{(0.129-2x)}{x} = 16.73\ x = 6.89 \times 10^{-3} M$

$[I_2]$ = $[Br_2]$ = 6.89 x 10^{-3} M

$[IBr]$ = 0.115 M

Exercise $7.E.16$*

Increasing the volume of the container will decrease pressure. This will cause the reaction to shift towards the greater number of moles of gas.

a. In this reaction, the number of moles of gas on both sides of the equation is equal (2 moles of gas on the left and 2 moles on the right). Since there is no difference in the number of moles of gas, increasing the volume will not affect the equilibrium concentrations of reactants and products.

b. There are 3 moles of gas on the left (reactants) and only 2 moles of gas on the right (products). Increasing the volume will decrease the pressure, and the reaction will shift to the left, favouring the formation of more reactants to increase the total number of gas moles.

c. In this reaction, the left side has no gas molecules (only solid $BaSO_3$) and the right side has 1 mole of gas, SO_2. Increasing the volume will decrease the pressure, causing the reaction to shift to the right, favouring the formation of more products (more gas).

d. There are more moles of gas on the right side compared with the left side, so the reaction will shift right, forming more products.

Exercise $7.E.17$*

To maximize the yield of products, we can change the volume of the container to shift the equilibrium position according to Le Châtelier's Principle. Changing the volume affects the pressure of a gas-phase system:

- Increasing volume lowers pressure and favours the side with more gas molecules.
- Decreasing volume raises pressure and favours the side with fewer gas molecules.

a. There are no moles of gas on the reactant side, while there are 5 moles of gas on the product side. Increasing the volume will decrease the pressure, causing the equilibrium to shift toward the side with more gas molecules (the product side). Therefore, to maximize the product yield, the volume should be increased.

b. On the reactant side, there are 3 moles of gas, and on the product side, there are 2 moles of gas. Decreasing the volume increases the pressure, which shifts the equilibrium toward the side with fewer gas molecules (the product side). Therefore, to maximize the product yield, the volume should be decreased.

Exercise $7.E.18$*

When the temperature increases, the system will shift to absorb the added heat, in accordance with Le Châtelier's Principle. If the reaction is endothermic (ΔH > 0), heat can be treated as a reactant, and the equilibrium will shift toward the products (right) to absorb the added heat. Conversely, if the reaction is exothermic

(ΔH < 0), heat acts as a product, and the equilibrium will shift toward the reactants (left) to counteract the increase in temperature.

a. ΔH > 0, shifts right (towards products)

b. ΔH > 0, shifts right (towards products)

c. ΔH < 0, shifts left (towards reactants)

d. ΔH < 0, shifts left (towards reactants)

Exercise $7.E.19$**

Add N_2 or H_2: increasing the concentration of either reactant will shift the reaction towards products, forming more hydrazine.

Decrease the container volume: a decrease in volume will increase pressure and shift the reaction towards fewer moles of gas. Since there are two moles of gas on the reactant side and 1 mole on the product side, the products will be favoured.

Heat the mixture: The reaction is endothermic, meaning it absorbs heat (heat can be considered to be a reactant). Increasing the temperature effectively adds heat to the system. According to Le Châtelier's Principle, the equilibrium will shift towards the products to absorb the added heat and produce more hydrazine.

Exercise $7.E.20$**

The equilibrium constant K_c depends only on temperature. Changes in concentration or pressure do not affect the value of K_c, although they may shift the position of equilibrium according to Le Châtelier's Principle.

a. Adding more solid CaO does not change the equilibrium position because the concentration of a solid is constant and does not appear in the equilibrium expression. K_c remains unchanged.

b. Removing some solid $CaSO_4$ does not change the equilibrium position. As with CaO, solids do not affect equilibrium position. K_c remains unchanged.

c. Removing a reactant shifts the reaction to the left, towards reactants to counteract its removal. K_c is unchanged, since only concentrations changed, not temperature. Once equilibrium is re-established, the equilibrium amounts of reactant and product will be different, but the value of K_c will be the same.

d. Adding reactant shifts the reaction to the right, towards products. K_c is unchanged, since concentrations changed, not temperature.

e. Increasing the volume decreases the pressure. The equilibrium will shift to the side with more gas molecules, which is the reactant side in this case. As before, the equilibrium amounts of reactant and product will be different, but the value of K_c will be the same.

Exercise $7.E.21$**

	$2\,NO_2\,(g)$ ⇌	$2\,NO\,(g)$ +	$O_2\,(g)$
Initial	1.5 atm	0 atm	0 atm
Change	- 2x	+2x	+x
Equilibrium	1.5 - 2x	2x	x

$K_p = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2} = \frac{(2x)^2(x)}{(1.50-2x)^2} = 6.5 \times 10^{-6}$

Assume 2x << 1.5 atm

$\frac{(2x)^2(x)}{(1.5)^2} = 6.5 \times 10^{-6}\ 4x^3 = 1.46 \times 10^{-5}\ x = 0.015\ \text{atm}$

Let's check the validity of our assumption:

$\frac{2(0.015\ atm)}{1.5\ atm} \times 100\% = 2.0\%$,

which is much smaller than 5%, confirming the assumption is valid.

$P_{NO_2} = 1.5 - 2x = 1.5\ \text{atm}\ P_{NO} = 2x = 0.030\ \text{atm}\ P_{O_2} = 0.015\ \text{atm}$

We can double-check these values by plugging back into the K_p expression:

$K_p = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2} = \frac{(0.030)^2(0.015)}{(1.5)^2} = 6.0 \times 10^{-6}$ which is close to the actual value, confirming our solution.

Exercise $7.E.22$**

a. $K_c = \dfrac{[CH3OH]}{[H2]^2[CO]}$

b. Adding more H_2 increases its concentration, which shifts the reaction to the right. At equilibrium, the concentration of H_2 will be higher, the concentration of CH_3OH will be higher (due to the shift towards products), and the concentration of CO will be lower (due to the shift towards products).

c. Removing CO decreases its concentration, which causes the reaction to shift left (toward the reactants) to produce more CO. At equilibrium, the concentration of CO will be lower than before it was removed, the concentration of H_2 will be higher (due to the shift towards reactants), and the concentration of CH_3OH will be lower (due to the shift towards reactants).

d. Adding more CH_3OH increases its concentration, which shifts the reaction to the left (towards the reactants). At equilibrium, the concentration of CH_3OH will be higher (due to the addition of CH_3OH) and the concentrations of H_2 and CO will be higher (due to the shift towards reactants).

e. The reaction is exothermic, so heat is a product. An increase in temperature will shift the reaction to the left to consume the added heat. At equilibrium, the concentration of H_2 and CO will be higher, and the concentration of CH_3OH will be lower.

f. A catalyst does not affect the equilibrium position. It only speeds up the rate at which equilibrium is reached.

Exercise $7.E.23$***

Calculation of K_c at 298 K:

$K_c = \frac{[B]}{[A]} = \frac{2.4}{0.80} = 3.0$

a. Since additional B (product) is added, the system will shift toward the reactants to consume some of the added B and produce more A. This can be seen by calculating the reaction quotient Q_c and comparing it to the equilibrium constant K_c:

$Q_c = \frac{[B]}{[A]} = \frac{3.2}{0.80} = 4.0$ Since $Q_c > K_c$, the reaction will shift to the left (towards the reactants) to restore equilibrium.

b.

A(g) ⇌	B (g)

Initial	0.80 M	3.2 M
Change	+x	-x
Equilibrium	0.80 + x	3.2 - x

$K_c = \frac{[B]}{[A]} = \frac{(3.2-x)}{(0.80+x)} = 3.0$

$K_c = \frac{[B]}{[A]} = \frac{(3.2-x)}{(0.80+x)} = 3.0\ 3.2 - x = 3.0(0.80 + x)\ 3.2 - x = 2.4 + 3.0x\ x = 0.20\ \text{M}$

[B] = 3.2 - x = 3.0 M

[A] = 1.0 M

Both concentrations of A and B are higher than in the original mixture, but K_C is unchanged.

c. $K_c = \frac{[B]}{[A]} = \frac{3.3}{0.70} = 4.7$

The increase in K_c with the increase in temperature indicates that the reaction is endothermic. According to Le Châtelier's Principle, increasing the temperature shifts the equilibrium toward the side that absorbs heat (the forward direction in this case), resulting in a higher value for K_c.

Exercise $7.E.24$***

The equilibrium constant expression is:

$K_p = P_{SO_2} = 9.65$

Although solids do not appear in the equilibrium expression, they are still part of the reaction. When the pressure of SO_2 is increased to 9.89 atm, the system is no longer at equilibrium. To re-establish equilibrium, the reaction shifts left, consuming some SO_2 and BaO and forming more BaSO_3:

	$\text{BaSO}_3\,(\text{s})$ ⇌	$\text{BaO}(\text{s}_0+$	$\text{SO}_2\,(\text{g})$
Initial	solid	solid	9.89 atm
Change	solid	solid	-x
Equilibrium	solid	solid	9.65 atm

Since $K_p = P_{SO_2} = 9.65$, the equilibrium pressure of SO_2 is 9.65 atm.

9.89 atm - 9.65 atm = 0.24 atm.

0.24 atm is the amount that reacted to reach equilibrium.

Converting to moles:

$n = \frac{PV}{RT} = \frac{(0.24\ atm)(10.0\ L)}{(0.08206\frac{L\cdot atm}{mol\ K})(355\ K)} = 0.082\ mol$

Since 1 mole of BaO is required to react with each mole of SO_2, we know that 0.082 mol of BaO also reacts:

$0.082\ mol\ \text{SO}_2\left(\frac{1\ mol\ \text{BaO}}{1\ mol\ \text{SO}_2}\right) = 0.082\ mol\ \text{BaO}\ 0.082\ mol\ \text{BaO}\ (153.33\ g/mol) = 13\ g\ \text{BaO}$

13 g of BaO reacts as the reaction returns to equilibrium.

Note: if less than 13 g of $\text{BaO}\,(\text{s})$ was initially present in the flask, equilibrium could not be re-established under these conditions.

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8: ACID-BASE EQUILIBRIA

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8.E: Acid-Base Equilibria (Exercises)

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8.1: Introduction

Blood, Balance, and Biochemistry: Acid–Base Equilibria in the Body

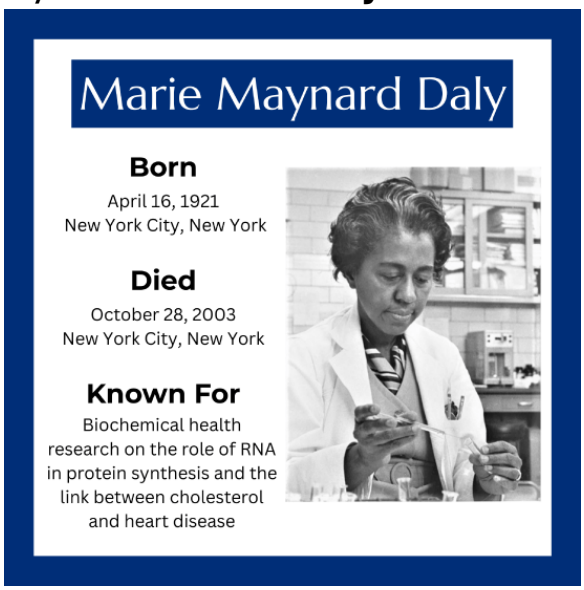


Figure 8.1.1**:** A graphic with basic facts about Marie Maynard Daly, the first Black woman to earn a PhD in chemistry in the US. Dr. Daly spent her career researching human biochemistry, leading her to make discoveries ranging from the structure of DNA to the role of cholesterol in human health. Image reproduced with permission from the Archives of the Albert Einstein College of Medicine; Ted Burrows, photographer.

Acid-base reactions are everywhere, from tooth erosion caused by soda to the action of household cleaners to the digestion of food. These reactions can also influence the behaviour of enzymes, affect the outcome of chemical reactions, and determine whether molecules carry a charge. Understanding how acids and bases behave, how they reach equilibrium, and how they can be controlled is essential to many areas of science and health.

Dr. Marie Maynard Daly, the first Black woman to earn a Ph.D. in chemistry in the United States, made groundbreaking contributions to biochemistry and human physiology. Though she did not study acid–base equilibria directly, much of her research depended on carefully controlling pH to study biological molecules under realistic conditions.

In the 1940s and 1950s, Daly investigated nucleic acids and protein synthesis, uncovering foundational insights into the roles of DNA and RNA. She was the first to show that the four nucleotide bases in DNA, adenine, guanine, thymine, and cytosine, were not present in equal amounts, an observation that laid the groundwork for the discovery of DNA's structure. She also co-authored one of the earliest studies linking RNA to protein synthesis, which was cited by James Watson in his Nobel Prize address. In all of this work, controlling pH was critical: enzymes function only under the right acid–base conditions, and small shifts can alter how biomolecules behave – even affecting whether they remain in solution or precipitate out of it.

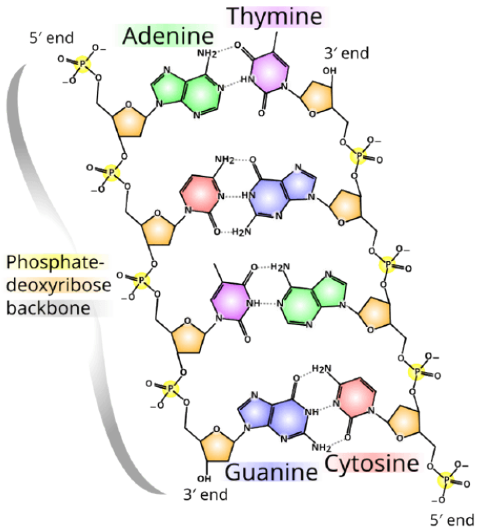


Figure 8.1.2**:** Depiction of the structure of DNA, highlighting the four different nucleotide bases that Daly mentioned in her work. Th phosphate groups (yellow) and deoxyribose sugars (orange) form covalent bonds that make up the "backbone" of DNA. In between ther four nucleotide bases form hydrogen bonds with each other in specific pairs: adenine (green) with thymine (pink) and guanine (blue) cytosine (red). Daly used pH to precipitate these nucleotides from solution so that they could be quantified, demonstrating that these bases could exist in unequal amounts; however, the amounts of adenine and thymine were equal to each other, as were the amounts guanine and cytosine, indicative of this specific pairing. Image reprinted from Wikimedia Commons with permission under Creative Cor license CC-BY.

Later in her career, Daly shifted her focus to cholesterol and heart disease, and then to creatine metabolism in muscle cells. Across these areas, acid–base chemistry played a supporting but essential role. Daly needed to control pH to mimic physiological conditions to ensure enzyme function, extract nucleotides and other components from cells, prevent degradation of components, and maintain constant conditions for electrophoresis experiments.

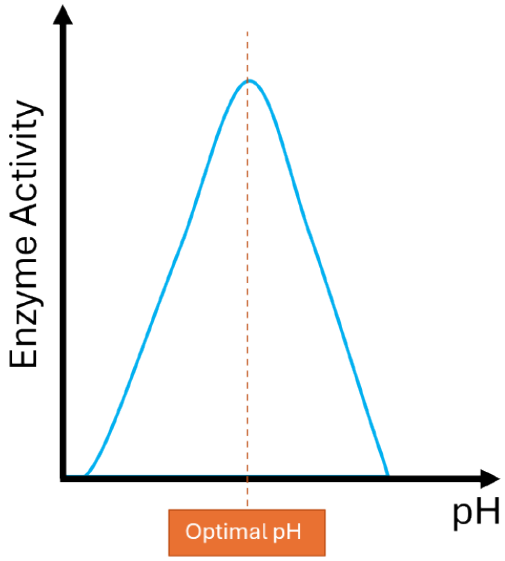


Figure 8.1.3**:** The relationship between enzyme function and pH. Enzymes operate most efficiently at a specific pH level. This efficiency off as the pH moves further and further away from this optimal value. Daly used this principle in her biochemical research to ensure tha enzymes she used or studied were operating optimally.

Acid-base chemistry is not only central to the chemistry curriculum. It is also vital to our understanding of how the human body

functions and how we treat disease. In this chapter, we will examine the same principles Dr. Daly relied on: what defines acids and bases, how to calculate and interpret pH, and the factors affecting acid-base equilibria.

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8.2: Brønsted-Lowry Acids and Bases

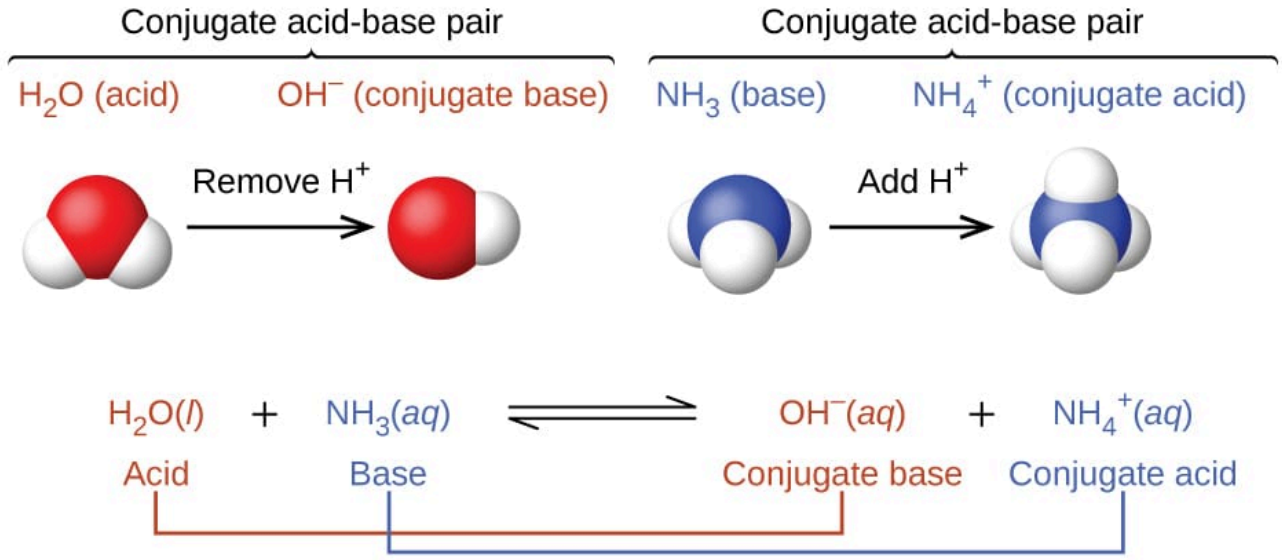
Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- 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 studied extensively. Svante Arrhenius provided an early definition in 1884, focusing on how these substances behave in water. He defined an acid as a compound that dissolves in water to produce hydrogen cations, $\mathrm{H^+}$, more accurately represented as hydronium ions, $\mathrm{H_3O^+}$, and a base as a compound that dissolves to produce hydroxide anions, $\mathrm{OH^-}$.

In 1923, Johannes Brønsted and Thomas Lowry proposed a broader definition based on the transfer of hydrogen ions ($\mathrm{H^+}$), often referred to as protons. According to this theory, an acid is a proton donor, and a base is a proton acceptor. An acid-base reaction, therefore, involves the transfer of a proton from the acid (donor) to the base (acceptor).

The concept of conjugate pairs helps explain Brønsted-Lowry acid-base reactions. When an acid donates a proton, it becomes its conjugate base, the species that can accept a proton in the reverse reaction. Similarly, when a base accepts a proton, it becomes its conjugate acid. Consider the reaction between water and ammonia. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, $\mathrm{OH^-}$, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, $\mathrm{NH_4^+}$, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base, accepting a proton from the ammonium ion, which acts as an acid.



Example 8.2.1

For each reaction identify the conjugate acid-base pair:

a. $\mathrm{HF\,(aq) + CO_3^{2-}\,(aq) \rightleftharpoons F^-\,(aq) + HCO_3^-\,(aq)}$

b. $\mathrm{H_2O\,(l) + NH_4^+\,(aq) \rightleftharpoons H_3O^+\,(aq) + NH_3\,(aq)}$

Solution

To identify the conjugate acid-base pairs:

- Look for the species that donates H^+ in the forward reaction and the base that forms in the products from the loss of the H^+.
- Look for the species that accepts H^+ in the forward reaction and the acid that forms in the products from accepting H^+.

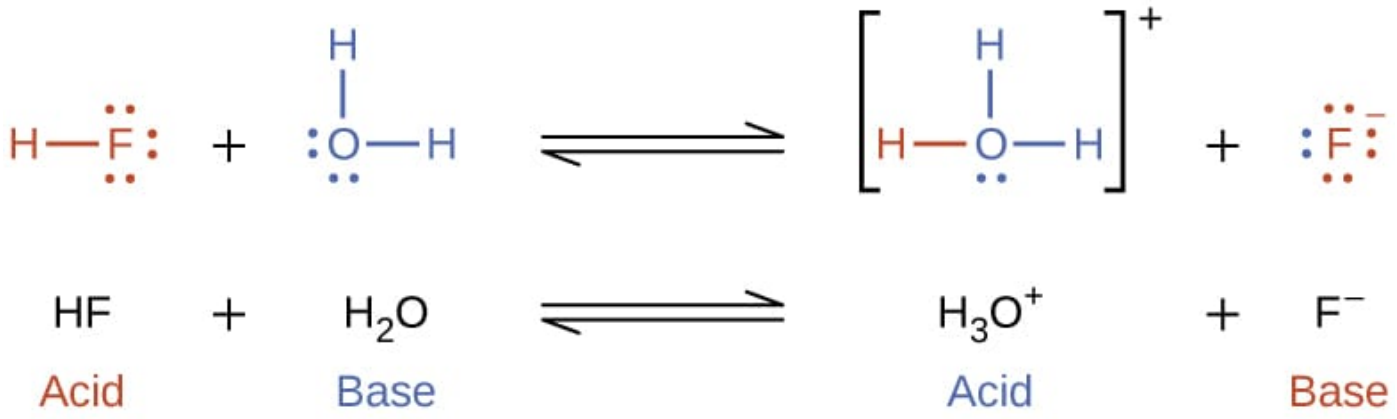
a. HF donates a proton to form F^-, therefore HF/F^- is a conjugate acid-base pair.

$CO_3{}^{2-}$ accepts a proton to form $HCO_3{}^-$, therefore $HCO_3{}^-/CO_3{}^{2-}$ is the other conjugate acid-base pair.

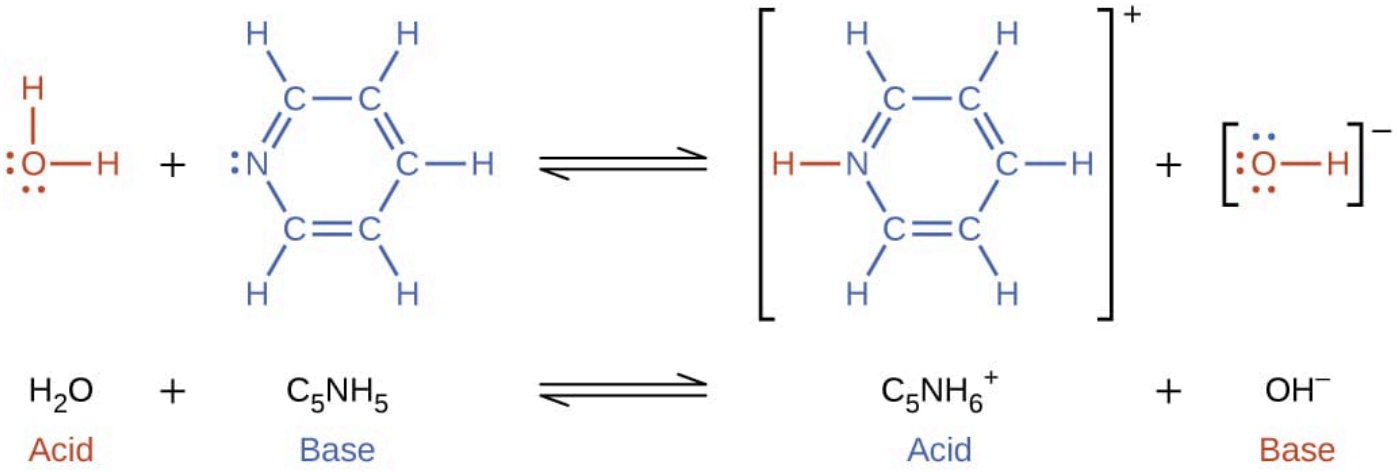
b. $NH_4{}^+$ loses a proton to form NH_3, therefore $NH_4{}^+/NH_3$ is a conjugate acid-base pair.

H_2O gains a proton to form H_3O^+, therefore H_3O^+/H_2O is a conjugate acid-base pair.

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:



Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:



As shown in these examples, water can act as both a base (e.g., with hydrogen fluoride) and an acid (e.g., with ammonia or pyridine). Substances that can either donate or accept a proton, depending on the reaction conditions, are called amphiprotic.

The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$\mathrm{HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)}$$

$$\mathrm{HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq)}$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents the reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously.

Example 8.2.2: Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$

b. as a base with HI

Solution

a. $\mathrm{HSO_3^-\,(aq) + OH^-\,(aq) \rightleftharpoons SO_3^{2-}\,(aq) + H_2O\,(l)}$
b. $\mathrm{HSO_3^-\,(aq) + HI\,(aq) \rightleftharpoons H_2SO_3\,(aq) + I^-\,(aq)}$

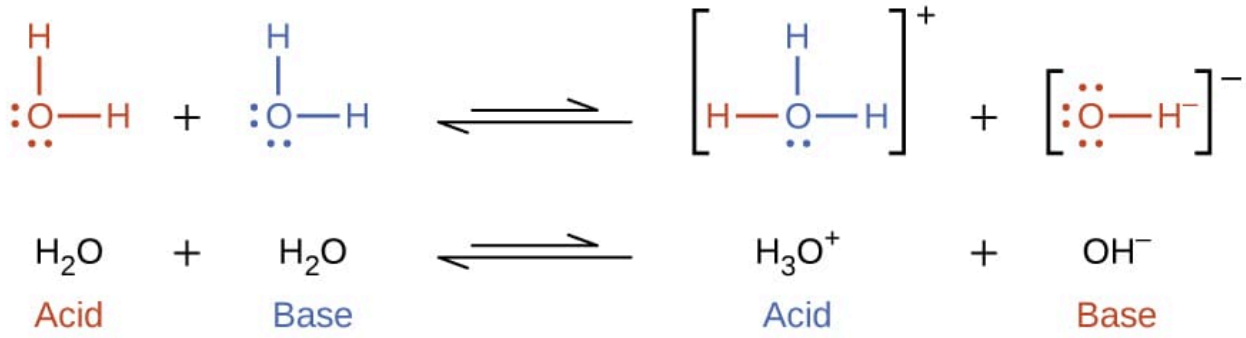
Exercise 8.2.1

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer available at the end of this section.

Since water is an amphiprotic substance, it can undergo an acid-base reaction with itself:



This equilibrium process is called autoionization, and it occurs to a very small extent in liquid water. At 25 °C, approximately two out of every billion water molecules are ionized:

$$\mathrm{2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)} \tag{8.2.1}$$

The equilibrium constant for this reaction, known as K_w, is given by:

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 298 \text{ K} \tag{8.2.2}$$

This value is important for understanding the neutral pH of water and will be used in equilibrium calculations later in this chapter.

In an acidic solution, $[\mathrm{H_3O^+}] > [\mathrm{OH^-}]$

In a basic solution, $[\mathrm{H_3O^+}] < [\mathrm{OH^-}]$

In a neutral solution, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$

The autoionization process is endothermic, so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature.

Example 8.2.3: Ion Concentrations in Pure Water

What are the hydronium ion and the hydroxide ion concentrations in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = x$. At 25 °C:

$$K_w = [H_3O^+]\,[OH^-] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

So:

$$x = [H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, $1.0 \times 10^{-7}\ M$.

Exercise 8.2.2

The ion product of water at 80 °C is 2.4 x 10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer available at the end of this section.

Example 8.2.4: The Inverse Relation between $[H_3O^+]$ and $[OH^-]$

In an aqueous solution, the hydronium ion concentration is $2.0 \times 10^{-6} M$. What is the concentration of hydroxide ion at 25 °C? Is the solution acidic, basic, or neutral?

Solution

Use the value of the ion-product constant for water at 25 °C to calculate the missing equilibrium concentration.

$$2\,\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

with $K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}]$.

$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9} M$

$[\mathrm{H_3O^+}] > [\mathrm{OH^-}]$, so the solution is acidic.

Exercise 8.2.3

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer available at the end of this section.

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, $[\mathrm{H_3O^+}]$, and the hydroxide ion, $\mathrm{OH^-}$ when it undergoes autoionization:

$$2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25°\mathrm{C}$$

Glossary

acid ionization
: A reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid.

amphiprotic
: A species that may either gain or lose a proton in a reaction.

autoionization
: A reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions.

base ionization
: A 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
: A proton donor.

Brønsted-Lowry base
: A proton acceptor.

conjugate acid
: A substance formed when a base gains a proton.

conjugate base
: A substance formed when an acid loses a proton.

conjugate pair
: A pair of Brønsted-Lowry acid and its conjugate base or base and its conjugate acid.

ion product of water (K_w)
: The equilibrium constant for the autoionization reaction of water.

Answers

Exercise 8.2.1

a. $\mathrm{H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)}$
b. $\mathrm{H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)}$

Exercise 8.2.2

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = 4.9 \times 10^{-7}\,M$$

Exercise 8.2.3

$$[H_3O^+] = 1 \times 10^{-11}\ M$$

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8.3: pH and pOH

Learning Objectives

- 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 seen in the previous section, hydronium $\mathrm{H_3O^+}$ and hydroxide $\mathrm{OH^-}$ ions are present in all aqueous solutions, including pure water. Their concentrations are inversely related through the ion product of water (K_w). These ion concentrations play a critical role in determining a solution's properties and the behaviour of its solutes. A solution is:

- Neutral when $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$,
- Acidic when $[\mathrm{H_3O^+}] > [\mathrm{OH^-}]$,
- Basic when $[\mathrm{H_3O^+}] < [\mathrm{OH^-}]$.

To handle quantities spanning many orders of magnitude, a logarithmic scale is often used. The p-function is defined as:

$$\mathrm{pX} = -\log\ \mathrm{X}$$

where X is the quantity of interest, and "log" is the base-10 logarithm.

The pH of a solution is the p-function of the hydronium ion concentration:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$$

Rearranging this equation gives the hydronium ion concentration:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}$$

Similarly, the pOH is defined for hydroxide ions:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

or equivalently:

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}}$$

The relationship between pH and pOH can be derived from the ion product of water (K_w):

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{8.3.1}$$

Taking the negative logarithm:

$$-\log K_w = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] - \log[\mathrm{OH^-}] \tag{8.3.2}$$

$$\mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH} \tag{8.3.3}$$

At 25 °C, $K_w = 1.0 \times 10^{-14}$, so $\mathrm{p}K_w = 14.00$. Thus, at this temperature:

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

As demonstrated previously, the hydronium ion concentration in pure water (or any neutral solution) is 1.0×10^{-7} M at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

$$\mathrm{pOH} = -\log\left[\mathrm{OH^-}\right] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

Thus:

- Acidic solutions have hydronium ion concentrations greater than $1.0 \times 10^{-7}\ \text{M}$ at 25 °C (pH < 7.00, pOH > 7.00).
- Basic solutions have hydronium ion concentrations less than $1.0 \times 10^{-7}\ \text{M}$ at 25 °C (pH > 7.00, pOH < 7.00).

Since the autoionization constant (K_w) is temperature-dependent, the pH ranges for acidic, neutral, and basic solutions differ at temperatures other than 25 °C. This distinction is important for processes that occur at other temperatures, such as enzyme reactions in warm-blooded organisms with temperatures from 36–40 °C. Unless otherwise specified, pH values are assumed to be at 25 °C (Table 8.3.1).

Table 8.3.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	pH < 7
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	pH = 7
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	pH > 7

Note on Significant Figures in pH Calculations

When using logarithms and antilogarithms in pH problems:

- The number of decimal places in a pH value equals the number of significant figures in the concentration.
  - Example: $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}\ \text{M}$ has 2 significant figures → pH = 7.00 (2 decimal places).
- When converting from pH back to concentration, the number of significant figures in $[\text{H}_3\text{O}^+]$ equals the number of decimal places in the pH.
  - Example: pH = 2.35 (2 decimal places) → $[\text{H}_3\text{O}^+] = 4.5 \times 10^{-3}\ \text{M}$

A full discussion can be found in Chapter 1.

Figure 8.3.1: shows the relationships between $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

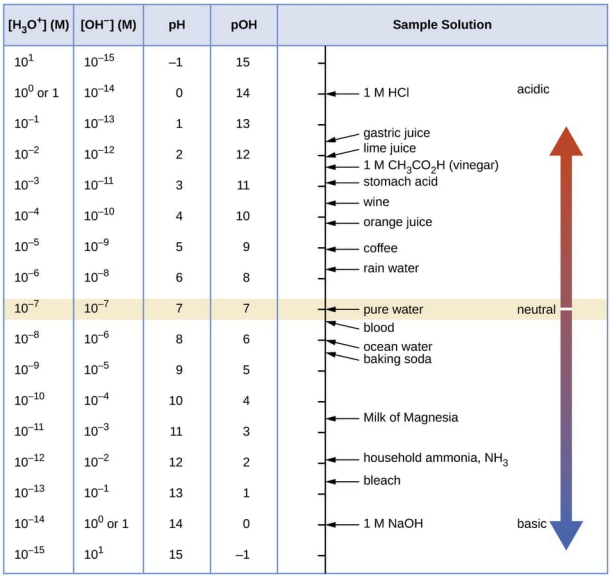


Figure 8.3.1: The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

Example 8.3.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} M?

Solution

$$\begin{aligned} \mathrm{pH} &= -\log\left[\mathrm{H_3O^+}\right] \\ &= -\log\left(1.2 \times 10^{-3}\right) \\ &= -(-2.92) = 2.92 \end{aligned}$$

The concentration has 2 significant figures, so the pH is reported with 2 decimal places to give 2 significant figures.

Exercise 8.3.1

Water exposed to air contains carbonic acid, $\mathrm{H_2CO_3}$, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_2CO_3\,(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved $\mathrm{CO_2}$ of 2.0×10^{-6} M, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer available at the end of this section.

Example 8.3.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned} \mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right] &= 7.3 \\ \log\left[\mathrm{H_3O^+}\right] &= -7.3 \\ \left[\mathrm{H_3O^+}\right] &= 10^{-7.3} = 5 \times 10^{-8}\,\mathrm{M} \end{aligned}$$

The pH has 1 significant figure, so there is only one significant figure in the concentration.

Exercise 8.3.2

Calculate the hydronium ion concentration of a solution with a pH of –1.07.

Answer available at the end of this section.

How Sciences Interconnect: Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved $\mathrm{CO_2}$ which reacts with water to form carbonic acid:

$$\begin{aligned} \mathrm{H_2O\,(l) + CO_2\,(g)} &\rightleftharpoons \mathrm{H_2CO_3\,(aq)} \\ \mathrm{H_2CO_3\,(aq) + H_2O\,(l)} &\rightleftharpoons \mathrm{H_3O^+\,(aq) + HCO_3^-\,(aq)} \end{aligned}$$

Acid rain refers to rainwater with a pH below 5, caused by the presence of additional acidic oxides such as $\mathrm{SO_2}$, $\mathrm{SO_3}$, NO, and $\mathrm{NO_2}$ that dissolve in rainwater to form sulfuric and nitric acids. For example, sulfuric acid forms via:

$$H_2O\,(l) + SO_3\,(g) \rightarrow H_2SO_4\,(aq)$$

$$H_2SO_4\,(aq) + H_2O(l) \rightarrow H_3O^+\,(aq) + HSO_4{}^-\,(aq)$$

Carbon dioxide is naturally present in the atmosphere as a metabolic byproduct from most organisms and from the combustion of organic materials (e.g., wood, fossil fuels). Sulfur oxides enter the atmosphere through volcanic eruptions, fossil fuel combustion (especially coal), and metal smelting operations. Nitrogen oxides are produced in internal combustion engines, where high temperatures allow atmospheric nitrogen and oxygen to react.

Acid rain has been especially problematic in industrial areas where sulfur and nitrogen oxides were historically released in large amounts. In North America and Europe through the 1980s, acid rain was responsible for forest dieback, soil degradation, and lake acidification — killing many aquatic species. It also causes corrosion of limestone and marble used in buildings and monuments (Figure 8.3.2). Regulations aimed at reducing emissions from industry and vehicles have led to significant decreases in acid rain and its effects in many parts of the world.



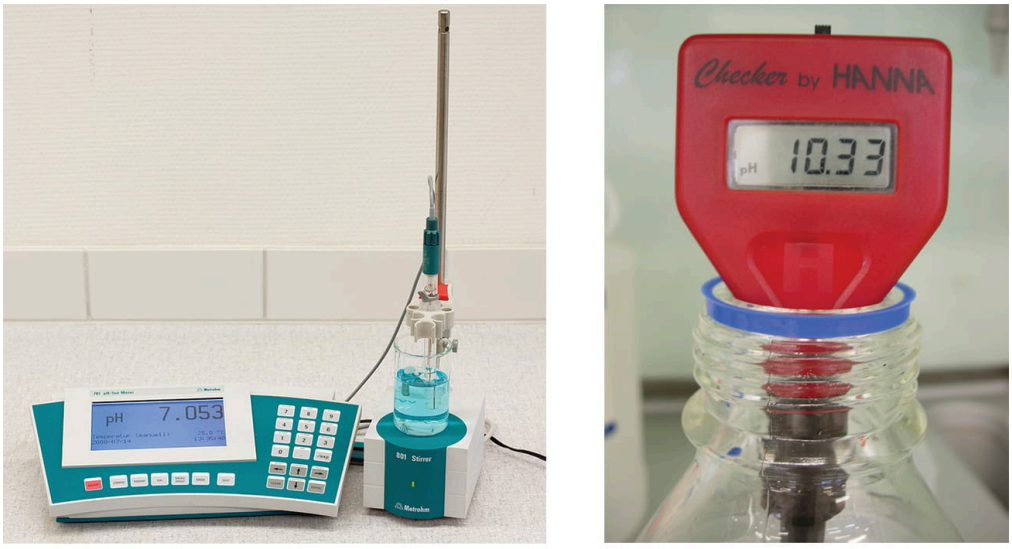
Figure 8.3.2: (a) Acid rain damages trees by leaching nutrients from the soil and weakening them against drought and pests.(b) Acidic precipitation also corrodes marble and limestone statues and buildings.
(credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

Exercise 8.3.3

The hydronium ion concentration of vinegar is approximately 4×10^{-3} M. What are the corresponding values of pOH and pH ?

Answer available at the end of this section.

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 8.3.3).



(a) (b)

Figure 8.3.3: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution can also be visually estimated using color-changing indicators (Figure 8.3.4), described in more detail later in this chapter.



(a) (b)

Figure 8.3.4: (a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

Summary

At 25 °C:

- Acidic solutions have hydronium ion concentrations, $[H_3O^+]$, greater than $1.0 \times 10^{-7}\ M$ and pH values less than 7.
- Basic solutions have hydroxide ion concentrations, $[OH^-]$, greater than $1.0 \times 10^{-7}\ M$ and pH values greater than 7.
- Neutral solutions have equal concentrations of hydronium and hydroxide ions, with a pH of 7.

The concentration of hydronium ions, $[H_3O^+]$, can be expressed as the pH of the solution:

$$\text{pH} = -\log[H_3O^+]$$

Similarly, the concentration of hydroxide ions, $[OH^-]$, can be expressed as the pOH of the solution:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-]$$

At 25 °C, the relationship between pH and pOH is:

$$\mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH}$$

Glossary

acidic aqueous solution
: A solution for which water is the solvent and the concentration of hydronium ions ($[H_3O^+]$) is greater than the concentration of hydroxide ions ($[OH^-]$), resulting a pH value less than 7.

basic aqueous solution
: A solution for which water is the solvent and the concentration of hydroxide ions ($[OH^-]$) is greater than the concentration of hydronium ions ($[H_3O^+]$), resulting a pH value greater than 7.

neutral aqueous solution
: A solution for which water is the solvent and the concentration of hydronium ions ($[H_3O^+]$) is equal to the concentration of hydroxide ions ($[OH^-]$), resulting a pH value of 7.

pH
: A logarithmic measure of the concentration of hydronium ions in a solution.

pOH
: A logarithmic measure of the concentration of hydroxide ions in a solution.

Answers

Exercise 8.3.1

$$\begin{aligned} pH &= -\log\left[\mathrm{H_3O^+}\right] \\ &= -\log\left(2.0 \times 10^{-6}\right) \\ &= 5.70 \end{aligned}$$

The concentration has 2 significant figures, so the pH is reported with 2 decimal places to give 2 significant figures.

Exercise 8.3.2

$$\begin{aligned} \mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right] &= -1.07 \\ \left[\mathrm{H_3O^+}\right] &= 10^{1.07} = 12\,\mathrm{M} \end{aligned}$$

The pH has 2 significant figures, so there are two significant figures in the concentration.

Exercise 8.3.3

$$\begin{aligned} \mathrm{pH} &= -\log\left[\mathrm{H_3O^+}\right] \\ &= -\log\left(4 \times 10^{-3}\ \mathrm{M}\right) \\ &= 2.4 \\ \mathrm{pOH} &= 14 - \mathrm{pH} = 14 - 2.40 = 11.6 \end{aligned}$$

The concentration has 1 significant figure, so the pH and pOH are reported with 1 decimal place to give 1 significant figure.

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8.4: Relative Strengths of Acids and Bases

Learning Objectives

- Relate the strength of acids and bases to their K_a and K_b values
- Recognize the complementary strength of conjugate acid-base pairs
- Predict the direction of an acid-base reaction on the strengths of conjugate acid-base pairs.

Acid and Base Ionization Constants

Acids and bases are classified by their strength, which is determined by their extent of ionization or dissociation in water. Strong acids and bases dissociate completely into ions, while weak acids and bases only partially ionize. Figure $8.4.1$ lists the most common strong acids and bases.

6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Figure $8.4.1$: Some of the common strong acids and bases are listed here.

The relative strengths of acids and bases may be quantified by measuring their equilibrium constants in aqueous solutions. For solutions of the same concentration, stronger acids ionize to a greater extent, yielding higher concentrations of hydronium ions than weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + A^-\,(aq)}$$

The acid-ionization constant is written

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are at equilibrium. Although water is a reactant in this reaction, it is a pure liquid and the solvent for the reaction; therefore $[\mathrm{H_2O}]$ is not included in the equation.

The magnitude of K_a reflects the strength of the acid. A larger K_a indicates greater equilibrium concentrations of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ relative to the concentration of the non-ionized acid, HA, signifying a stronger acid.

Since strong acids undergo complete ionization, at equilibrium, the concentration of HA is zero and the acid ionization constant is very large ($K_a >> 1$). Weak acids only partially ionize, so at equilibrium, much of the mixture is unreacted HA and their acid

ionization constants are small ($K_a << 1$).

To illustrate the relationship between K_a and acid strength, three acid ionization equations and K_a values are shown below:

$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + CH_3CO_2{}^-\,(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + NO_2{}^-\,(aq)} \qquad K_a = 4.5 \times 10^{-4}$$

$$\mathrm{HSO_4{}^-\,(aq) + H_2O\,(aq)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + SO_4{}^{2-}\,(aq)} \qquad K_a = 1.2 \times 10^{-2}$$

These values indicate that acid strength increases in the order:

$$\mathrm{CH_3CO_2H < HNO_2 < HSO_4{}^-}$$

Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is defined in terms of the composition of an equilibrium mixture:

$$\%\text{ ionization } = \frac{[\mathrm{H_3O^+}]_{eq}}{[\mathrm{HA}]_0} \times 100\%$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[\mathrm{A^-}] = [\mathrm{H_3O^+}]$). Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

Example 8.4.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125 M solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[\mathrm{H_3O^+}]_{eq}}{[\mathrm{HNO_2}]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[\mathrm{H_3O^+}] = 10^{-2.09} = 0.0081\mathrm{M}$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

Exercise 8.4.1

Calculate the percent ionization of a 0.10-M solution of acetic acid with a pH of 2.89.

Answer available at the end of this section.

Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions. Stronger bases ionize to a greater extent in solutions of the same concentration, producing higher concentrations of hydroxide ions $[\mathrm{OH^-}]$ than weaker bases. A stronger base has a larger ionization constant than a weaker base. For the reaction of a base, B:

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons HB^+\,(aq) + OH^-\,(aq)}$$

The base-ionization constant is written as

$$K_b = \frac{[\mathrm{HB^+}]\,[\mathrm{OH^-}]}{[\mathrm{B}]}$$

We can use K_b values to compare base strengths. The data show that base strength increases in the order: $\mathrm{NO_2^- < CH_2CO_2^- < NH_3}$

$$\mathrm{NO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HNO_2\,(aq) + OH^-\,(aq)} \qquad K_b = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3\ CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3\ CO_2\ H\,(aq) + OH^-\,(aq)} \qquad K_b = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \qquad K_b = 1.8 \times 10^{-5}$$

As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\%\ \text{ionization} = \left(\frac{[\mathrm{OH^-}_{eq}]}{[\mathrm{B}]_0}\right) \times 100\%$$

but will vary depending on the base ionization constant and the initial concentration of the solution.

Example 8.4.2

Ammonia ($\mathrm{NH_3}$) is a weak base that partially ionizes in water according to the following equilibrium equation:

$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)}$$

A "0.10 M solution" of ammonia has a hydroxide ion ($\mathrm{OH^-}$) concentration of 1.3 × 10^{-3} M at 25 °C. Calculate the percent ionization of ammonia in this solution.

Solution

Initial concentration of ammonia: $[\mathrm{NH_3}]_{\text{initial}}$ = 0.10 M

Hydroxide ion concentration at equilibrium: $[\mathrm{OH^-}]_{\text{eq}}$ = 1.3×10^{-3} M

From the stoichiometry of the reaction, **for every mole of $\mathrm{NH_3}$ that "ionizes", 1 mole of $\mathrm{OH^-}$ is produced**.

So, the amount of $\mathrm{NH_3}$ that "ionized" is equal to the amount of $\mathrm{OH^-}$ formed:

$[\mathrm{NH_3}]_{\text{ionized}} = [\mathrm{OH^-}] = 1.3 \times 10^{-3}$ M

$$\%\ \text{ionization} = \left(\frac{[\mathrm{OH^-}_{eq}]}{[\mathrm{NH_3}_0]}\right) \times 100\% = \frac{1.3 \times 10^{-3} M}{0.10 M} \times 100\% = 1.3\%$$

To simplify comparisons, ionization constants are often expressed as their negative logarithms:

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

A smaller pK_a or pK_b corresponds to a stronger acid or base, respectively.

Relative Strengths of Conjugate Acid-Base Pairs

The strength of an acid and its conjugate base are connected. Let's look at the equilibria of the conjugate acid-base pair HA / $\mathrm{A^-}$ to see how they are related. Here is the reaction of acid HA with water:

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)}$$

and it's acid dissociation constant (K_a):

$$K_a = \frac{[H3O^+][A^-]}{[HA]}$$

Here is the reaction of the conjugate base of HA, $\mathrm{A^-}$, with water:

$$\mathrm{A^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + HA\,(aq)}$$

and it's base dissociation constant (K_b):

$$K_b = \frac{[HA][OH-]}{[A-]}$$

Adding these equations gives the autoionization of water:

$$\cancel{HA(aq)} + \mathrm{H_2O\,(l)} + \cancel{A^-(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \cancel{A^-(aq)} + \mathrm{OH^-\,(aq)} + \cancel{HA(aq)}$$

$$\mathrm{2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)}$$

Recall from the previous chapter that the equilibrium constant for a summed reaction equals the product of the equilibrium constants for the individual reactions:

$$K_a \times K_b = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

This shows that the product of the ionization constants for a conjugate acid-base pair equals the ion product of water, K_w:

$$K_a \times K_b = K_w$$

From this, we derive the reciprocal relationship:

$$K_a = \frac{K_w}{K_b}$$

or

$$K_b = \frac{K_w}{K_a}$$

This inverse proportionality means the stronger an acid (larger K_a), the weaker its conjugate base (smaller K_b), and vice versa. Figure $8.4.2$ shows this inverse relationship. Notice that acid strength increases from right to left, while conjugate base strength increases from left to right.

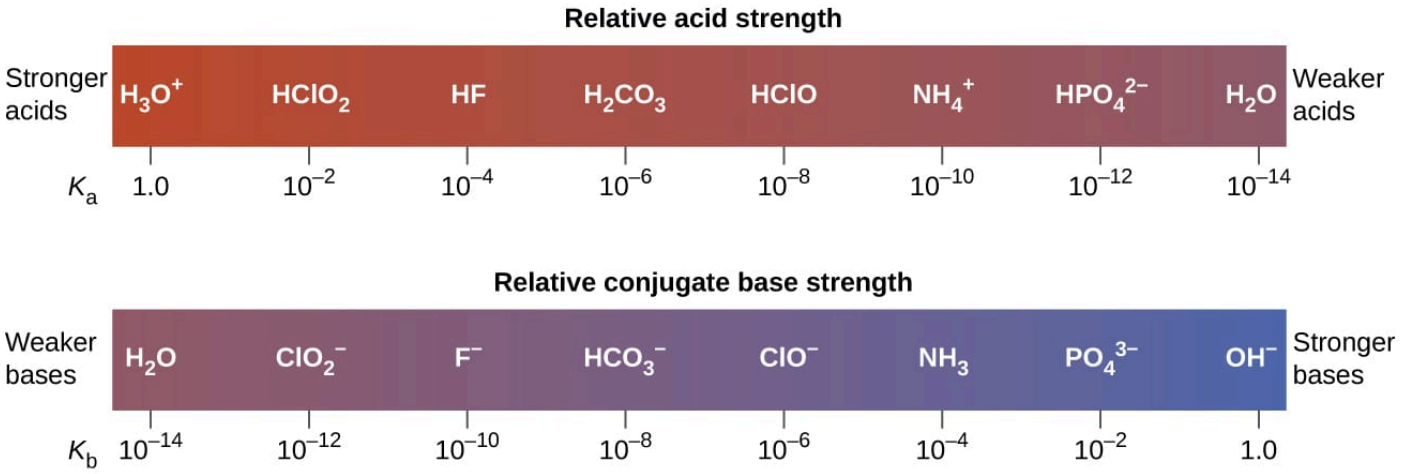


Figure 8.4.2: Relative strengths of several conjugate acid-base pairs are shown.

Figure 8.4.3 shows the strength of conjugate acid–base pairs relative to water, which is highlighted in each column. Acids listed below water are very weak and do not ionize significantly in water. Weak acids, located between water and hydronium ion, partially ionize, while strong acids, listed above hydronium ion, ionize completely in aqueous solutions.

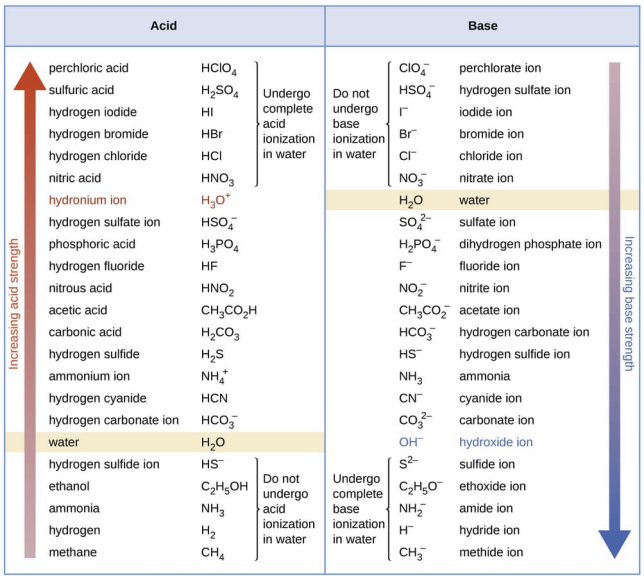


Figure 8.4.3: This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

All strong acids are completely ionized in water. In aqueous solutions, any acid stronger than hydronium ion (H_3O^+) donates all of its protons to water, resulting in the formation of H_3O^+. Consequently, acids like HCl, HNO_3, and $HClO_4$ appear equally strong in water, as they all fully ionize to produce H_3O^+. This phenomenon is known as the leveling effect, where H_3O^+ is the strongest acid that can exist in water. To differentiate the strengths of such strong acids, they must be dissolved in solvents less basic than water, such as ethanol.

The right column (Figure 8.4.3) shows the conjugate bases of each acid. The strongest bases are at the bottom of the list. As with the acid column, the species listed above water are very weak bases and do not ionize significantly in water. Species between water and hydroxide ion, OH^- are weak bases that partially ionize, while species below hydroxide ion are strong bases that completely ionize in water, yielding hydroxide ions.

A comparison of the acid and base columns shows the reciprocal relationship between conjugate acid-base pairs. For example, the conjugate bases of strong acids (at the top of the table) are very weak, because a strong acid has a very large K_a meaning its conjugate base has a very small K_b:

$$\text{strong acid: } K_a \gg 1 \quad \text{conjugate base: } K_b = \frac{K_w}{K_a} \ll 1$$

Similarly, the conjugate acids of strong bases (with $K_b >> 1$) are very weak, with $K_a << 1$.

Example 8.4.3: Calculating Ionization Constants for Conjugate Acid-Base Pairs

The K_a for nitrous acid $\mathrm{HNO_2}$ is 7.1 x 10^{-4}. What is K_b for the nitrite ion, $\mathrm{NO_2}^-$?

Solution

The conjugate base of $\mathrm{HNO_2}$ is $\mathrm{NO_2}^-$; K_b for $\mathrm{NO_2}^-$ can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_b yields

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.4 \times 10^{-11}$$

Exercise 8.4.2

Determine the relative acid strengths of $\mathrm{NH_4}^+$ and HClO by comparing their ionization constants. The ionization constant of HClO is 2.9×10^{-8}. The ionization constant of $\mathrm{NH_4}^+$ is not given, but the ionization constant of its conjugate base, $\mathrm{NH_3}$, is 1.8×10^{-5}.

Answer available at the end of this section.

Acid and Base Strength and Reaction Direction

The net direction of an acid-base reaction depends on the relative strengths of the acids and bases involved. Consider the general equilibrium:

$$\mathrm{HX\,(aq) + Y^-\,(aq) \rightleftharpoons X^-\,(aq) + HY\,(aq)}$$

In the forward direction, HX acts as the acid, donating a proton H^+ to Y^-, which acts as the base. In the reverse direction, HY is the acid, donating a proton to X^-, the base. The stronger acid, HX or HY, is better at giving up a proton, while the stronger base (X^- or Y^-) is better at accepting a proton. Because of the inverse relationship between the strength of acids and their conjugate bases, the stronger acid is always paired with the weaker conjugate base, and the stronger base is always paired with the weaker conjugate acid. As a result, the reaction proceeds to a greater extent in the direction where the stronger acid and base form the weaker acid and base.

Now, consider this specific reaction:

$$\mathrm{HNO_2\,(aq) + NH_3\,(aq) \rightleftharpoons NO_2{}^-\,(aq) + NH_4{}^+\,(aq)}$$

In the forward direction, $\mathrm{HNO_2}$ is the acid, while in the reverse direction, $\mathrm{NH_4}^+$ is the acid. Referring to Figure 8.4.3, $\mathrm{HNO_2}$ is a stronger acid than $\mathrm{NH_4}^+$. Given the inverse relationship between acids and their conjugate bases, $\mathrm{NH_3}$ is a stronger base than $\mathrm{NO_2}^-$. Thus, the net reaction proceeds in the forward direction, where the stronger acid $\mathrm{HNO_2}$ and stronger base $\mathrm{NH_3}$ react to form the weaker acid $\mathrm{NH_4}^+$ and weaker base $\mathrm{NO_2}^-$. This corresponds to an equilibrium constant (K_c) greater than 1.

Example \({8{.}4{.}\eatSpaces{4} \endSpaces}

Use Figure 8.4.3 to predict the net direction of the reaction and if K_c is less than or greater than 1 for the following reactions (assuming equal concentrations of all species.)

a. $\mathrm{HF\,(aq) + CO_3{}^{2-}\,(aq) \rightleftharpoons F^-\,(aq) + HCO_3{}^-\,(aq)}$

b. $\mathrm{HCN\,(aq) + NO_2{}^-\,(aq) \rightleftharpoons HNO_2\,(aq) + CN^-\,(aq)}$

Solution

a. HF is a stronger acid than $\mathrm{HCO_3{}^-}$, so the net direction is forward and $K_c > 1$.

b. $\mathrm{HNO_2}$ is a stronger acid than HCN, so the net direction is reverse and $K_c < 1$.

Summary

The strength of an acid is expressed by its acid-ionization constant, which is defined by the reaction:

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)}$$

with the acid-ionization constant written as:

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

Similarly, the strength of a base is expressed its base-ionization constant, which is defined by the reaction:

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons HB^+\,(aq) + OH^-\,(aq)},$$

with the base-ionization constant written as:

$$K_b = \frac{[\mathrm{HB^+}]\,[\mathrm{OH^-}]}{[\mathrm{B}]}$$

Strong acids and strong bases ionize completely in water, resulting in very large K_a and K_b values. Weak acids and weak bases only ionize slightly, with K_a and K_b values much less than 1.

When an acid donates a proton, it forms its conjugate base. Likewise, when a base accepts a proton, it forms its conjugate acid. A stronger acid always has a weaker conjugate base, and vice versa.

The net direction of an acid-base reaction favours the side where the stronger acid and base form the weaker acid and base.

Glossary

acid ionization constant (K_a)
: The equilibrium constant for the ionization of a weak acid.

base ionization constant (K_b)
: The equilibrium constant for the ionization of a weak base.

dissociation
: A physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution.

percent ionization
: A measure of acid or base strength; ratio of the concentration of the ionized acid/base to the initial acid/base concentration, multiplied by 100.

strong acid
: An acidic substance that dissociates completely into ions in water.

strong base
: A basic substance that dissociates completely into ions in water.

Answers

Exercise 8.4.1

1.3% ionized

Exercise 8.4.2

K_a for $\mathrm{NH_4^+}$ is 5.6×10^{-10}

$\mathrm{NH_4^+}$ is a weaker acid than HClO.

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8.5: pH of Strong Acids and Strong Bases

Learning Objectives

- Calculate the pH of strong acid and strong base solutions

As mentioned in the last section, strong acids and strong bases completely ionize in water.

Strong Acids

Strong acids completely ionize in water, which can be represented with a single arrow:

$$\mathrm{HA\,(aq) + H_2O\,(l)\ \rightarrow H_3O^+\,(aq) + A^-\,(aq)}$$

Here, water acts as a base reacting with the acid HA. The ion $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion $\mathrm{H_3O^+}$ is the conjugate acid of water. By definition, a strong acid completely ionizes in water, producing 100% $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

For a strong acid, $[\mathrm{H_3O^+}] = [\mathrm{A^-}] \approx [\mathrm{HA}]_{\mathrm{initial}}$

Note: In extremely dilute solutions (less than 1×10^{-7} M), the autoionization of water significantly affects pH.

To calculate the pH of a strong acid solution, we use the initial concentration of the acid to determine the $[\mathrm{H_3O^+}]$, as shown in the example below:

Example 8.5.1

Calculate the pH of a solution with $1.23 \times 10^{-4}\ \mathrm{M\ HCl}$.

Solution

HCl is a strong acid, so it completely ionizes, as represented by the reaction:

$$\mathrm{HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

$$[\mathrm{H_3O^+}] = [\mathrm{HA}]_{\mathrm{initial}} = 1.23 \times 10^{-4}\mathrm{M}$$

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.23 \times 10^{-4}) = 3.910$$

Note: there are three decimal places in the pH because there are three significant figures in the concentration.

Exercise 8.5.1

What is the pH of a solution containing 1.234 M $[\mathrm{HNO_3}]$?

Answer available at the end of this section.

Strong Bases

Strong bases behave similarly to strong acids and are completely ionized in solution. For example, KOH dissolves in water in the reaction:

$$\mathrm{KOH} \rightarrow \mathrm{K^+ + OH^-}$$

Relative to the number of strong acids, there are fewer strong bases and most are alkali hydroxides. When $\mathrm{Ca(OH)_2}$ dissolves in water, the ionization reaction is as follows:

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{2+} + 2\,OH^-}$$

Because of the stoichiometry of calcium hydroxide, upon dissociation, the concentration of $\mathrm{OH^-}$ will be twice the concentration of $\mathrm{Ca^{2+}}$:

$$[\mathrm{OH^-}] = 2[\mathrm{Ca^{2+}}]$$

Example 8.5.2

Calculation pOH and pH of a 0.10 M NaOH solution.

Solution

$$\mathrm{NaOH} \rightarrow \mathrm{Na^+ + OH^-}$$

$$[\mathrm{OH^-}] = 0.10\,\mathrm{M}$$

$$\mathrm{pOH} = -\log\,[\mathrm{OH^-}] = -\log\,(0.10\,\mathrm{M}) = 1.00$$

$$\mathrm{pH} = 14 - \mathrm{pOH} = 13.00$$

Note: there are two decimal places in the pH and pOH because there are two significant figures in the concentration.

Example 8.5.3

Calculate the pOH and pH of a solution containing $1.23 \times 10^{-4}\ \mathrm{M}\ \mathrm{Ca(OH)_2}$.

Solution

Based on complete ionization of

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{+2} + 2\,OH^-}$$

$$\begin{aligned}[\mathrm{OH^-}] &= 2 \times 1.23 \times 10^{-4} \\ &= 2.46 \times 10^{-4}\ M \\ \mathrm{pOH} &= -\log(2.46 \times 10^{-4}) \\ &= 3.609\end{aligned}$$

$$\mathrm{pH} = 14 - \mathrm{pOH} = 10.391$$

Note: there are three decimal places in the pH and pOH because there are three significant figures in the concentration.

Exercise 8.5.2

A solution contains 0.013 M calcium hydroxide, $\mathrm{Ca(OH)_2}$. Calculate the pOH.

Answer available at the end of this section.

Summary

Strong acids and bases fully ionize in water. Therefore, their initial concentrations directly determine the concentrations of $\mathrm{H_3O^+}$ or $[\mathrm{OH^-}]$, allowing straightforward calculation of pH or pOH.

Answers

Exercise 8.5.1

$[\mathrm{H_3O^+}] = [\mathrm{HNO_3}]_{\text{initial}} = 1.234\mathrm{M}$

$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.234) = -0.09132$

Note: pH values can be negative for highly concentrated strong acids.

There are four decimal places in the pH because there are four significant figures in the concentration.

Exercise 8.5.2

[OH^-] = 2(0.013 M) = 0.026 M

pOH = -log[OH^-]=-log(0.026M) = 1.59

Note: there are two decimal places in the pH and pOH because there are two significant figures in the concentration.

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8.6: pH of Weak Acids and Bases

Learning Objectives

- Carry out equilibrium calculations for weak acid and weak base systems
- Calculate the pH of weak acids and weak bases given initial concentrations and K values.

Unlike strong acids and bases, which fully dissociate in water, weak acids and bases only partially ionize. This partial ionization means that the concentrations of hydronium ions $\mathrm{H_3O^+}$ for weak acids and hydroxide ions $\mathrm{OH^-}$ for weak bases depend on the specific substance and its ionization constant. To determine the pH of solutions containing weak acids or bases, it's necessary to perform equilibrium calculations, as introduced in the previous chapter. These calculations will be illustrated through examples throughout this section.

Acid-Base Equilibrium Calculations

We'll begin by calculating acid and base ionization constants, K_a and K_b, from known equilibrium concentrations.

Example 8.6.1: Determination of K_a from Equilibrium Concentrations

Acetic acid, the main ingredient in vinegar (Figure 8.6.1), gives its sour taste. At equilibrium, a solution contains $[\mathrm{CH_3CO_2H}] = 0.0787\ \mathrm{M}$ and $[\mathrm{H_3O^+}] = [\mathrm{CH_3CO_2{}^-}] = 0.00118\ \mathrm{M}$. What is the value of K_a for acetic acid?



Figure 8.6.1: Vinegar contains acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

Write the balanced equation and the corresponding expression for the acid-ionization constant:

$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + CH_3CO_2{}^-\,(aq)}$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{CH_3CO_2{}^-}]}{[\mathrm{CH_3CO_2H}]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Exercise 8.6.1

The hydrogen sulfate ion (HSO_4^-) acts as a weak acid in aqueous solutions:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

An equilibrium mixture has the following concentrations:

- $[H_3O^+] = 0.027\ M$
- $[HSO_4^-] = 0.29\ M$
- $[SO_4^{2-}] = 0.13\ M$

What is K_a for HSO_4^-?

Answer available at the end of this section.

Example 8.6.2: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050\ M$, $[C_8H_{10}N_4O_2H^+] = 5.0 \times 10^{-3}\ M$, and $[OH^-] = 2.5 \times 10^{-3}\ M$?

Solution

Write the balanced equation and the corresponding expression for the base-ionization constant:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

$$\begin{aligned} K_b &= \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} \\ &= \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{(0.050)} \\ &= 2.5 \times 10^{-4} \end{aligned}$$

Exercise 8.6.2

The hydrogen phosphate ion (HPO_4^{2-}) acts as a weak base in aqueous solution:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$

An equilibrium mixture has the following concentrations:

- $[OH^-] = 1.3 \times 10^{-6}\ M$
- $[H_2PO_4^-] = 0.042\ M$
- $[HPO_4^{2-}] = 0.341\ M$

What is K_b for HPO_4^{2-}?

Answer available at the end of this section.

Example 8.6.3: Determination of K_a or K_b from pH

The pH of a 0.0516 M solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

The concentration of nitrous acid given is a formal concentration, meaning it refers to the amount initially added to solution, not accounting for any changes due to ionization. This initial concentration is used as the starting point in an ICE table (Initial, Change, Equilibrium).

Although a small amount of $\mathrm{H_3O^+}$ is always present in water due to autoionziation ($1 \times \times 10^{-7}$ M), this contribution is negligible compared to the amount formed by the weak acid and can be ignored.

The pH gives us the equilibrium concentration of hydronium ion, since it results from ionization of $\mathrm{HNO_2}$:

$$[\mathrm{H_3O^+}] = 10^{-2.34} = 0.0046 \text{ M}$$

Setting up an ICE table using this value:

	$\mathrm{HNO_2}$ + $\mathrm{H_2O}$ ⇌	$\mathrm{H_3O^+}$ +	$\mathrm{NO_2^-}$
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	−0.0046	+0.0046	+0.0046
Equilibrium concentration (*M*)	0.0470	0.0046	0.0046

Use these equilibrium concentrations to calculate K_a:

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{NO_2^-}]}{[\mathrm{HNO_2}]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 8.6.3

The pH of a solution of household ammonia, a 0.950 M solution of $\mathrm{NH_3}$, is 11.612. What is K_b for $\mathrm{NH_3}$?

$\mathrm{NH_3\,(aq)}$ +		$\mathrm{H_2O\,(l)}$ ⇌	$\mathrm{NH_4^+\,(aq)}$ +	$\mathrm{OH^-\,(aq)}$
Initial	0.950 M	X	0 M	0 M
Change	- x		+x	+x
Equilibrium	0.950 M- x		x	x

Answer available at the end of this section.

In the previous examples, we focused on calculating the acid and base ionization constants (K_a and K_b) from known equilibrium concentrations. Now, we will apply these constants to determine the concentrations of species at equilibrium. This involves using initial concentrations and equilibrium constants to solve for unknown values, often employing ICE (Initial, Change, Equilibrium) tables.

Example 8.6.4: Calculating Equilibrium Concentrations in a Weak Acid Solution

Formic acid, $\mathrm{HCO_2H}$, is one of the irritants that causes the stinging sensation from ant bites and stings (Figure 8.6.2).



Figure 8.6.2: The pain of some ant bites and stings is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH of a 0.534 M formic acid solution?

$$\mathrm{HCO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_2^-\,(aq)} \quad K_a = 1.8 \times 10^{-4}$$

Solution

Set up an ICE table to track the changes in concentrations as equilibrium is established:

	$\mathrm{HCO_2H}$ + $\mathrm{H_2O}$ $\rightleftharpoons$	$\mathrm{H_3O^+}$ +	$\mathrm{HCO_2^-}$
Initial concentration (*M*)	0.534	~0	0
Change (*M*)		+*x*	+*x*
Equilibrium concentration (*M*)	0.534 −*x*	*x*	*x*

Substitute equilibrium concentration terms into the K_a expression:

$$K_a = 1.8 \times 10^{-4} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{HCO_2^-}]}{[\mathrm{HCO_2H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Because the value of K_a is small and the initial concentration is relatively large, the change in concentration (x) is small compared to the initial concentration. We can simplify our calculations by assuming that x is negligible relative to the initial concentration $(x << 0.534\mathrm{M})$:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solving the equation for x yields:

$$x^2 = 0.534 \times \left(1.8 \times 10^{-4}\right) = 9.6 \times 10^{-5}$$
$$x = \sqrt{9.6 \times 10^{-5}}$$
$$= 9.8 \times 10^{-3} M$$

To determine if the simplifying assumption is appropriate, we can use the 5% rule:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} (1.8\% \text{ of } 0.534M)$$

Since 1.8% is less than 5%, the assumption is valid.

As defined in the ICE table, x is equal to the equilibrium concentration of hydronium ion:

$$x = \left[\mathrm{H_3O^+}\right] = 0.0098 \text{ M}$$

Finally, the pH is calculated to be

$$\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right] = -\log(0.0098) = 2.01$$

Example 8.6.5: Calculating Equilibrium Concentrations in a Weak Base Solution

What is the concentration of hydroxide ion, the pOH, and the pH of a 0.25 M solution of trimethylamine, a weak base?

$$(\mathrm{CH_3})_3\mathrm{N}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons (\mathrm{CH_3})_3\mathrm{NH^+}\,(\mathrm{aq}) + \mathrm{OH^-}\,(\mathrm{aq}) \quad K_b = 6.3 \times 10^{-5}$$

Solution

Start with an ICE table to track changes in concentration:

	$(CH_3)_3N$ + H_2O ⇌ $(CH_3)_3NH^+$ + OH^-			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.25 + (−*x*)		0 + *x*	~0 + *x*

Substitute the equilibrium concentration into the K_b expression:

$$K_b = \frac{\left[(\mathrm{CH_3})_3\mathrm{NH^+}\right]\left[\mathrm{OH^-}\right]}{\left[(\mathrm{CH_3})_3\mathrm{N}\right]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assume $x \ll 0.25$:

$$\frac{x^2}{0.25} = 6.3 \times 10^{-5}$$
$$x = 4.0 \times 10^{-3} \text{ M}$$

Because this is less than 5% of 0.25 M, the assumption is valid:

$$\frac{4.0 \times 10^{-3}\ \text{M}}{2.5\ \text{M}} \times 100\% = 1.6\%$$

The value of x represents the equilibrium concentration of hydroxide ion:

$$[\text{OH}^-] = x = \left(4.0 \times 10^{-3}\text{M}\right)$$

Calculate the pOH:

$$\text{pOH} = -\log\left(4.0 \times 10^{-3}\right) = 2.40$$

Then calculate the pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

In some cases, the strength of the weak acid or base and its initial concentration result in appreciable ionization. While ICE tables still work for these situations, the simplifying assumption that $x << [\text{initial}]$ is no longer valid. In these cases, we must solve the full quadratic equation. The example below demonstrates this approach.

Example 8.6.6: Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, NaHSO_4, is used in some household cleansers as a source of the HSO_4^- ion, a weak acid. What is the pH of a 0.50 M solution of HSO_4^-?

$$\text{HSO}_4^-\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+\,(\text{aq}) + \text{SO}_4^{2-}\,(\text{aq}) \quad K_a = 1.2 \times 10^{-2}$$

Solution

Start with an ICE table:

	HSO_4^-	+ H_2O ⇌	H_3O^+	+ SO_4^{2-}
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	−*x*		+*x*	+*x*
Equilibrium concentration (*M*)	0.50 − *x*		*x*	*x*

Substitute the equilibrium concentration terms into the K_a expression:

$$K_a = 1.2 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+]\,[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If the assumption that $x \ll 0.5$ is made, simplifying and solving the above equation yields

$$x = 0.077\ \text{M}$$

This value of x is not significantly less than 0.50 M. Checking the assumption:

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

Because this is greater than 5%, the assumption is not valid, and we must solve the full quadratic equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^2$$

Writing the equation in quadratic form gives

$$x^2 + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.012 \pm \sqrt{(0.012)^2 - 4(-0.0060)}}{2} = 0.072 \text{ and } -0.083\text{M}$$

In this calculation, we obtain two solutions: 0.072 M and -0.083 M. Since negative concentrations are not physically meaningful in this context, we discard the negative root. Thus, the hydronium ion concentration is 0.072 M.

$$x = [H_3O^+] = 0.072 \text{ M}$$

$$\text{pH} = -\log [H_3O^+] = -\log(0.072) = 1.14$$

Exercise 8.6.4

Calculate the pH in a 0.010 M solution of caffeine, a weak base.

$$C_8H_{10}N_4O_2\,(aq) + H_2O\,(l) \rightleftharpoons C_8H_{10}N_4O_2H^+\,(aq) + OH^-\,(aq) \quad K_b = 2.5 \times 10^{-4}$$

Answer available at the end of this section.

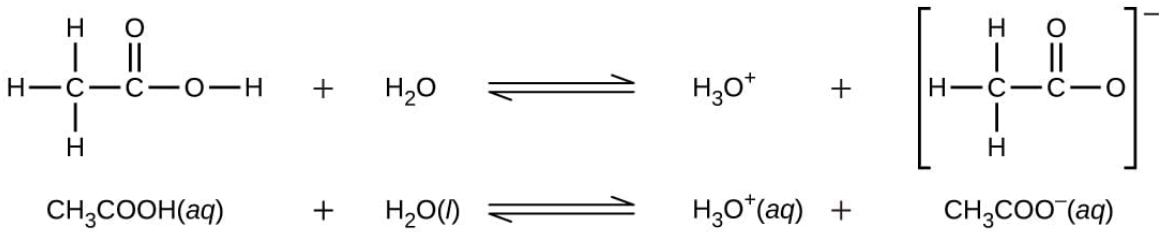
Polyprotic acids and bases

Polyprotic Acids and Bases

Acids are classified by the number of ionizable protons (hydrogen atoms that can be donated as (H^+)). Acids such as HCl, HNO_3, and HCN, which contain one ionizable hydrogen atom per molecule, are called monoprotic acids. Their ionization reactions in water are:

$$HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$
$$HNO_3\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + NO_3{}^-\,(aq)$$
$$HCN\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CN^-\,(aq)$$

Although acetic acid (CH_3COOH contains four hydrogen atoms, it is considered monoprotic because only the hydrogen atom from the carboxyl group ($-COOH$) is ionizable:



Similarly, monoprotic bases can accept only one proton.

Polyprotic Acids

Polyprotic acids have more than one ionizable proton per molecule and undergo stepwise ionization, each with its own acid dissociation constant (K_a). The first ionization occurs to a greater extent than subsequent ones. For example, carbonic acid undergoes the following ionizations:

$$\mathrm{H_2\ CO_3\,(aq) + H_2\ O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + HCO_3{}^-\,(aq)} \qquad \text{(First ionization)}$$

with

$$K_{a1} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{HCO_3{}^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

$$\mathrm{HCO_3{}^-\,(aq) + H_2\ O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + CO_3{}^{2-}\,(aq)} \qquad \text{(Second ionization)}$$

with

$$K_{a2} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{CO_3{}^{2-}}]}{[\mathrm{HCO_3{}^-}]} = 4.7 \times 10^{-11}$$

Here, K_{a1} is approximately 10^4 times larger than K_{a2}, so $\mathrm{HCO_3{}^{2-}}$contributes far more to $\mathrm{H_3O^+}$ in solution.

Phosphoric acid is a polyprotic acid with three ionizable protons:

$$\mathrm{H_3PO_4\,(aq) + H_2O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + H_2\ PO_4{}^-\,(aq)} \quad K_{a1} = 7.5 \times 10^{-3} \qquad \text{(First ionization)}$$

$$\mathrm{H_2PO_4{}^-\,(aq) + H_2O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + HPO_4{}^{2-}\,(aq)} \quad K_{a2} = 6.2 \times 10^{-8} \qquad \text{(Second ionization)}$$

$$\mathrm{HPO_4{}^{2-}\,(aq) + H_2O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + PO_4{}^{3-}\,(aq)} \quad K_{a3} = 4.2 \times 10^{-13} \qquad \text{(Third ionization)}$$

Each successive ionization occurs to a lesser extent, as reflected by the decreasing K_a values.

Polyprotic Bases

Polyprotic bases can accept more than one proton. For example, the carbonate ion $\mathrm{CO_3{}^{2-}}$ is a diprotic base:

$$\mathrm{H_2\ O\,(l) + CO_3{}^{2-}\,(aq)\ \rightleftharpoons HCO_3{}^-\,(aq) + OH^-\,(aq)} \quad K_{b1} = 2.1 \times 10^{-4}$$

$$\mathrm{H_2\ O\,(l) + HCO_3{}^-\,(aq)\ \rightleftharpoons H_2\ CO_3\,(aq) + OH^-\,(aq)} \quad K_{b2} = 2.3 \times 10^{-8}$$

Similar to acids, each successive step in protonation is less favorable, as shown by the decreasing K_b values.

Note:
Calculations involving polyprotic acids and bases are beyond the scope of CHM 135H.

Summary

Weak acids and weak bases ionize only slightly in water. To calculate the pH of their solutions, we analyze equilibrium concentrations. Typically, the extent of ionization is so small that it is negligible compared to the initial concentration, simplifying calculations. Polyprotic acids have more than one ionizable proton, and their successive K_a values differ by several orders of magnitude. Similarly, polyprotic bases can accept more than one proton. However, calculations involving polyprotic acids and bases are beyond the scope of this course.

Glossary

monoprotic acid
: An acid containing one ionizable hydrogen atom per molecule.

polyprotic acid
: An acid with more than one ionizable proton per molecule, undergoing stepwise ionization

polyprotic base
: A base that can accept more than one proton, undergoing stepwise protonation.

Answers

Exercise 8.6.1

$K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.027M)(0.13M)}{0.29M} = 1.2 \times 10^{-2}$

Exercise 8.6.2

$K_b = \frac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{(1.3\times10^{-6}M)(0.042M)}{0.341M} = 1.6 \times 10^{-7}$

Exercise 8.6.3

$$\mathrm{pOH} = 14.00 - \mathrm{pH} = 2.388$$

\[\ce{[OH-] = 10^{-2.388} = 4.09 x 10^-3 M = x} \nonumber\]

$$\begin{aligned} K_b &= \frac{[NH_4^+][OH^-]}{[NH_3]} \\ &= \frac{x^2}{(0.950 - x)} \\ &= \frac{(4.09 \times 10^{-3})^2}{(0.950 - 4.09 \times 10^{-3})} \\ &= 1.77 \times 10^{-5} \end{aligned}$$

Exercise 8.6.4

	$C_8H_{10}N_4O_2\,(aq)$ +	$H_2O\,(l)$ ⇌	$C_8H_{10}N_4O_2H^+\,(aq)$ +	\(\ce{OH-(aq)\)
Initial	0.010 M	X	0 M	0 M
Change	- x		+x	+x
Equilibrium	0.010 M- x		x	x

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(x)(x)}{(0.010 - x)} = 2.5 \times 10^{-4}$$

$$\begin{aligned} x^2 &= 2.5 \times 10^{-4}(0.010 - x) \\ x^2 + 2.5 \times 10^{-4}x - 2.5 \times 10^{-6} &= 0 \\ x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-2.5 \times 10^{-4} \pm \sqrt{(2.5 \times 10^{-4})^2 - 4(1)(-2.5 \times 10^{-6})}}{2(1)} \\ &= \frac{-2.5 \times 10^{-4} \pm 0.00326}{2} \\ &= \begin{cases} 0.0015 \\ -0.0018 \end{cases} \end{aligned}$$

The negative root gives a negative concentration which does not make sense chemically, so we can reject that root.

$$[OH^-] = [C_8H_{10}N_4O_2H^+] = 0.0015\,\mathrm{M}$$
$$[C_8H_{10}N_4O_2] = 0.010\,\mathrm{M} - 0.0015 = 0.0085\,\mathrm{M}$$
$$\mathrm{pOH} = -\log[OH^-] = -\log(0.0015) = 2.82$$
$$\mathrm{pH} = 14 - \mathrm{pOH} = 11.18$$

Finally, checking to see if the equilibrium values give the known K_b, we have:

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(0.0015)(0.0015)}{(0.0085)} = 2.6 \times 10^{-4}$$

This calculated K_b value is close to the given value, confirming the accuracy of our computations.

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8.7: Acid-Base Properties of Salt Solutions

Learning Objectives

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the pH and the concentrations of the various species in a salt solution

Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may react with water as acids or bases. A salt solution may be acidic, basic, or neutral, depending on the relative acid–base strengths of the ions.

For example, dissolving ammonium chloride in water yields:

$$\mathrm{NH_4Cl\,(s)} \rightarrow \mathrm{NH_4{}^+\,(aq)} + \mathrm{Cl^-\,(aq)}$$

The ammonium ion is the conjugate acid of the weak base ammonia, $\mathrm{NH_3}$. Its ionization in water is:

$$\mathrm{NH_4{}^+\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{NH_3\,(aq)} \quad K_a = K_w/K_b$$

Since $\mathrm{NH_3}$ is a weak base (K_b = 1.8 x 10^{-5}), its conjugate acid ($\mathrm{NH_4{}^+}$) is a weak acid (K_a = 5.6 x 10^{-10}).

The chloride ion is the conjugate base of the strong acid hydrochloric acid. Its ionization reaction is:

$$\mathrm{Cl^-\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{HCl\,(aq)} + \mathrm{OH^-\,(aq)}$$

Because HCl is a strong acid (very large K_a), its conjugate base $\mathrm{Cl^-}$ is an extremely weak base and does not appreciably react with water.

Dissolving ammonium chloride in water yields a solution of weak acid cations ($\mathrm{NH_4{}^+}$) and inert anions $\mathrm{Cl^-}$, resulting in an acidic solution.

Example 8.7.1: Calculating the pH of an Acidic Salt Solution

Anilinium chloride, $\mathrm{C_6H_5NH_3Cl}$, is a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 M solution of anilinium chloride? The K_b for aniline, the conjugate base of the anilinium ion, is 4.3 x 10^{-10}.

$$\mathrm{C_6H_5NH_3{}^+\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{C_6H_5NH_2\,(aq)}$$

Solution

Calculate the K_a for anilinium ion:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Set up an ICE table:

	$C_6H_5NH_3^+$ + H_2O ⇌	$C_6H_5NH_2$ +	H_3O^+
Initial concentration (*M*)	0.233	0	~0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.233 - x$	x	x

Substitute equilibrium concentrations into the K_a expression:

$$K_a = \frac{[C_6H_5NH_2]\,[H_3O^+]}{[C_6H_5NH_3^+]}$$

$$2.3 \times 10^{-5} = \frac{(x)(x)}{0.233 - x}$$

Assuming $x \ll 0.233$, the equation is simplified and solved for x:

$$2.3 \times 10^{-5} = \frac{x^2}{0.233}$$

$$x = 0.0023\ \text{M}$$

Checking the assumption:

$$\frac{0.0023\ \text{M}}{0.233\ \text{M}} \times 100\% = 0.99\%$$

Since this is less than 5%, the assumption is valid.

Calculate pH:

$$\text{pH} = -\log\left[H_3O^+\right] = -\log(0.0023) = 2.64$$

Exercise 8.7.1

What is the hydronium ion concentration in a 0.100 M solution of ammonium nitrate, NH_4NO_3? The K_b of NH_3 is 1.8 x 10^{-5}.

Answer available at the end of this section.

Salts with Basic Ions

Let's look at a salt that contains a basic ion. Consider sodium acetate dissolving in water:

$$NaCH_3CO_2\,(s) \rightleftharpoons Na^+\,(aq) + CH_3CO_2^-\,(aq)$$

The sodium ion does not react appreciably with water—it is inert and does not affect pH.

The acetate ion, $CH_3CO_2^-\,(aq)$, is the conjugate base of acetic acid, CH_3CO_2H, so it can accept a proton in water:

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3\ CO_2\ H\,(aq) + OH^-\,(aq) \quad K_b = K_w/K_a$$

Because acetic acid is a weak acid, (K_a = 1.8 x 10^{-5}), its conjugate base is a weak base (K_b = 5.6 x 10^{-10}).

Dissolving sodium acetate in water yields a solution of inert cations (Na^+) and basic anions ($CH_3CO_2^-$), resulting in a basic

solution.

Example 8.7.2: pH of salt solution

What is the pH of a 0.083 M solution of NaCN? The K_a of HCN is 6.2 x 10^{-10}.

Solution

$$\mathrm{CN^-\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{HCN\,(aq) + OH^-\,(aq)} \quad K_b = K_w/K_a = 1.6 \times 10^{-5}$$

$\mathrm{CN^-\,(aq)}$ \(\ce{+}\)	$\mathrm{H_2O\,(l)}$ ⇌		$\mathrm{HCN\,(aq)}$ \(\ce{+}\)	$\mathrm{OH^-\,(aq)}$
Initial	0.083 M	X	0 M	0 M
Change	- x		+x	+x
Equilibrium	0.083 M- x		x	x

Substituting the values into the K_b expression gives

$$K_b = \frac{[\mathrm{HCN}][\mathrm{OH^-}]}{[\mathrm{CN^-}]} = \frac{(x)(x)}{(0.083\mathrm{M} - x)} = 1.6 \times 10^{-5}$$

Assuming $x << 0.083$ M:

$$\frac{(x)(x)}{(0.083\ \mathrm{M})} = 1.6 \times 10^{-5}$$
$$x = 1.15 \times 10^{-3}\mathrm{M}$$

Checking the assumption:

$$\frac{1.15 \times 10^{-3}}{0.083\ \mathrm{M}} \times 100\% = 1.4\%$$

Since this is less than 5%, the assumption is valid.

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log\left(1.15 \times 10^{-3}\mathrm{M}\right) = 2.94; \mathrm{pH} = 14 - \mathrm{pOH} = 11.06$$

Salts with Acidic and Basic Ions

Some salts contain both acidic and basic ions. The resulting pH depends on the relative strengths of these ions. Salts with amphiprotic ions (which can act as either an acid or a base) also follow this logic.

To determine the solution's character (acidic, basic, or neutral), compare the K_a and K_b values for the relevant ion.

Example 8.7.3: Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. KBr
b. $\mathrm{NaHCO_3}$ (For $\mathrm{H_2CO_3}$: K_{a1} = 4.5 x 10^{-7}, K_{a2} = 4.7 x 10^{-11})

c. Na_2HPO_4 (For H_3PO_4: K_{a1} = 7.3 x 10^{-3}, K_{a2} = 6.2 x 10^{-8}, K_{a3} = 4.2 x 10^{-13})
d. NH_4F ((For NH_3: K_b = 1.8 x 10^{-5}; For HF: K_a = 6.8 x 10^{-4})

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

(a) The K^+ cation is inert and will not affect pH. The bromide ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

(b) The Na^+ cation is inert and will not affect the pH of the solution; while the HCO_3^- anion is amphiprotic. The K_a of HCO_3^- is 4.7×10^{-11}, and its K_b is:

$$\frac{1.0 \times 10^{-14}}{4.5 \times 10^{-7}} = 2.2 \times 10^{-8}$$

Since $K_b > K_a$, HCO_3^- is a stronger base than acid, so the solution is basic.

(c) The Na^+ cation is inert and will not affect the pH of the solution, while the HPO_4^{2-} anion is amphiprotic. The K_a of HPO_4^{2-} is 4.2×10^{-13}, and its K_b is:

$$\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$$

Because $K_b \gg K_a$, the solution is basic.

(d) The NH_4^+ ion is acidic (conjugate acid of the weak base NH_3) and the F^- ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of NH_4^+ is 5.6×10^{-10} and the K_b of F^- is 1.5×10^{-11}, NH_4^+ is a strong acid than F^- is a base, so the solution is acidic, since $K_a > K_b$.

Exercise 8.7.2

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. K_2CO_3
b. $CaCl_2$
c. KH_2PO_4, (For H_3PO_4: K_{a1} = 7.3 x 10^{-3}, K_{a2} = 6.3 x 10^{-8}, K_{a3} = 4.2 x 10^{-13})
d. $(NH_4)_2CO_3$ (For NH_3: K_b = 1.8 x 10^{-5}; For H_2CO_3: K_{a1} = 4.5 x 10^{-7}, K_{a2} = 4.7 x 10^{-11})

Answer available at the end of this section.

Summary

Salt solutions can be acidic, basic, or neutral, depending on how their ions interact with water:

- If the cation is a weak acid, it increases $[H_3O^+]$ giving an acidic solution.
- If the anion is a weak base, it increases $[OH^-]$ giving a basic solution.
- If both ions are inert, the solution is neutral.
- If one ion is acidic and one ion is basic, compare K_a and K_b:
  - K_a > K_b gives an acidic solution
  - K_b > K_a gives a basic
  - K_a = K_b gives a neutral solution

Glossary

salts

Ionic compounds composed of cations and anions, either of which may react with water as acids or bases.

Answers

Exercise 8.7.1

	$NH_4^+(aq)$ \(\text{+}\)	$H_2O(l)$ ⇳	$NH_3(aq)$ \(\text{+}\)	$H_3O^+(aq)$
Initial	0.10 M	X	0 M	0 M
Change	- x		+x	+x
Equilibrium	0.10 M- x		x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{0.10 - x}$$

Assuming $x \ll 0.10M$, the equation is simplified and solved for x:

$$5.6 \times 10^{-10} = \frac{x^2}{0.10}$$

$$x = 7.5 \times 10^{-6}\ \text{M}$$

Checking the assumption:

$$\frac{7.5 \times 10^{-6}}{0.10M} \times 100\% = 0.0075\%$$

Since this is less than 5%, the assumption is valid.

$[H_3O^+] = 7.5 \times 10^{-6}\ \text{M}$

Exercise 8.7.2

a. The K^+ cation is inert and will not affect pH. ${CO_3}^{2-}$ can act as a weak base, accepting a proton. The solution is basic.

${CO_3}^{2-} + H_2O \rightleftharpoons {HCO_3}^{1-} + OH^-$

b. The Ca^{2+} cation is inert and will not affect pH. The chloride ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

c. The K^+ cation is inert and will not affect pH. Consider ${H_2PO_4}^-$ acting as an acid or a base.

${H_2PO_4}^- + H_2O \rightleftharpoons {HPO_4}^{2-} + H_3O^+ K_{a2} = 6.3 \times 10^{-8}$

${H_2PO_4}^- + H_2O \rightleftharpoons H_3PO_4 + OH^- K_b = \frac{K_w}{K_{a1}} = 1.4 \times 10^{-12}$

Since $K_a > K_b$, the solution is acidic.

d. ${NH_4}^+$ can act as a weak acid:

$${NH_4}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) K_a = \frac{K_w}{K_b} = 5.6 \times 10^{-10}$$

${CO_3}^{2-}$ can act as a weak base:

${CO_3}^{2-} + H_2O \rightleftharpoons {HCO_3}^{1-} + OH^- K_b = \frac{K_w}{K_{a2}} = 2.1 \times 10^{-4}$

Since $K_b > K_a$, the solution is basic.

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8.8: Molecular Structure and Acid-Base Behavior

Learning Objectives

- Predict the relative strength of acids based on their molecular structure

The strength of an acid depends on how easily it can donate $\mathrm{H^+}$, which means breaking the bond to its acidic proton. We will examine atomic and molecular properties that explain trends in acid strength for:

- Binary acids $\mathrm{H{-}E}$
- Oxoacids $\mathrm{O}_m\mathrm{E(OH)}_n$

Binary Acids

The strength of a binary acid $\mathrm{H{-}E}$ depends mainly on two factors:

1. Bond strength $\mathrm{E{-}H}$
2. Electronegativity of the nonmetal E

Of these, bond strength is typically more important. A stronger E bond is less likely to break and release $\mathrm{H^+}$. Consequently, stronger bonds yield weaker acids, and weaker bonds yield stronger acids. This trend appears clearly with the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
$\mathrm{H{-}X}$ Bond Energy (kJ/mol)	570	432	366	298
$pK_a{}^*$	3.20	−6.1	−8.9	−9.3

Note: In aqueous solution, HCl, HBr, and HI all ionize completely, so their relative strengths cannot be measured experimentally using water as the solvent. This is because water "levels" any strong acid to the same strength (i.e., water fully reacts with the strong acid to form the conjugate base and hydronium ion). To distinguish among the strengths of strong acids, a solvent that is a weaker base than water must be used, and the pK_a values must be measured outside of the standard aqueous environment.

As we move from HF to HI, the bond energy decreases because the larger halogen atoms have poorer orbital overlap with hydrogen's 1s orbital. The weaker the $\mathrm{H{-}X}$ bond, the stronger the acid: $\mathrm{HF} < \mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}$.

In general, as the atom size increases down a group, the atom forms a longer, weaker H–E bond, and the acid strength increases. For example:

$$\mathrm{H_2O}\ (\mathrm{pK_a} = 14.00) < \mathrm{H_2S}\ (7.05) < \mathrm{H_2Se}\ (3.89) < \mathrm{H_2Te}\ (2.6)$$

Across a period, the $\mathrm{H{-}E}$ bond strength changes less, so electronegativity becomes the dominant factor. The more electronegative the element E, the more polar the $\mathrm{H{-}E}$ bond, making it easier for a water molecule's partially negative oxygen to pull $\mathrm{H^+}$ away. Consequently, acid strength increases with electronegativity across a period.

For second-row elements, the order of increasing acidity (for removal of one proton) is:

$$\mathrm{CH_4} < \mathrm{NH_3} < \mathrm{H_2O} < \mathrm{HF}$$

In the third row, the trend is:

$$\mathrm{SiH_4} < \mathrm{PH_3} < \mathrm{H_2S} < \mathrm{HCl}$$

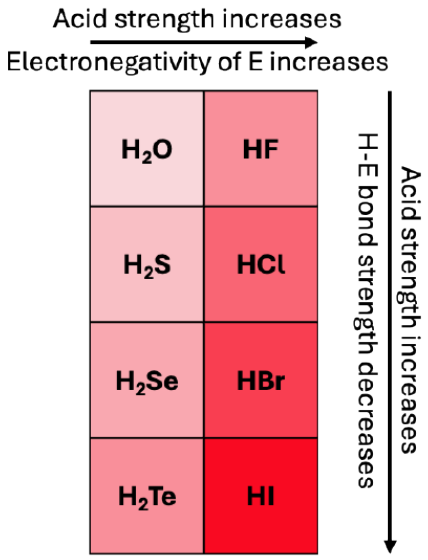
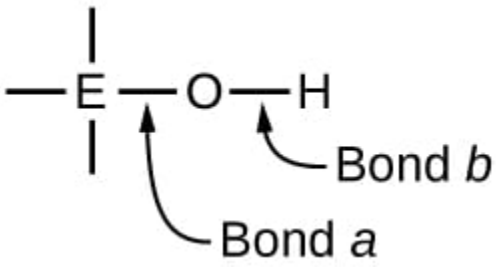


Figure 8.8.1: The figure shows trends in the strengths of binary acids and bases.

Oxoacids

Oxoacids are composed of hydrogen, oxygen, and a third element (E) as depicted in the image below. These acids have the general formula $\mathrm{O}_m\mathrm{E}(\mathrm{OH})_n$, where E is a central atom bonded to one or more oxygen atoms, and at least one OH group provides the acidic hydrogen. Because the acidic proton in an oxoacid is always bonded to an oxygen atom, bond length is not a controlling factor in acidity (unlike in binary acids).



Two factors determine the strength of the oxoacid:

1. Electronegativity of the central nonmetal, E

2. Number of oxygen atoms bond to E

When comparing oxoacids with the same number of O atoms, the acid strength increases with the electronegativity of the central atom, E. For instance, in the haolgen oxoacids, HOCl, HOBr, and HOI, the difference in halogen electronegativities leads to acidity variations over three orders of magnitude:

HOX	Electronegativity of X	pK_a
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

A more electronegative central atom draws electron density away from the O—H bond, making that bond weaker and more polar. This makes it easier for hydrogen to dissociate as H^+.

For oxoacids with different numbers of O atoms, the acid strength increases with the number of O atoms. Oxygen is a very electronegative element. Additional oxygen atoms withdraw electron density which increases the polarity of the $\mathrm{O{-}H}$ bond and facilitates the release of $\mathrm{H^+}$. For example, as shown in Figure 2, nitric acid $\mathrm{HNO_3}$) is a stronger acid than nitrous acid ($\mathrm{HNO_2}$) and sulfuric acid ($\mathrm{H_2SO_4}$) is a stronger acid than sulfurous acid ($\mathrm{H_2SO_3}$).

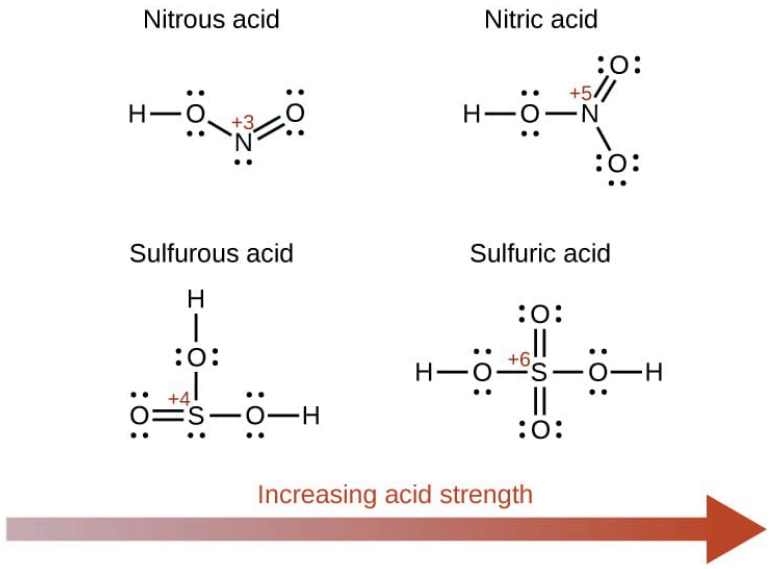


Figure $8.8.2$: As the number of O atoms around the central atom E increases, the acidity also increases.

Figure $8.8.3$ uses electrostatic potential maps to illustrate changes in electron density as the number of oxygen atoms increases from HClO to $\mathrm{HClO_4}$.

- Blue regions correspond to low electron density,
- Red regions correspond to high electron density.

As more oxygen atoms bond to the central atom, the hydrogen appears bluer (more positive character). The increased polarity of the $\mathrm{O{-}H}$ makes it easier to lose $\mathrm{H^+}$ and thus increases acid strength.

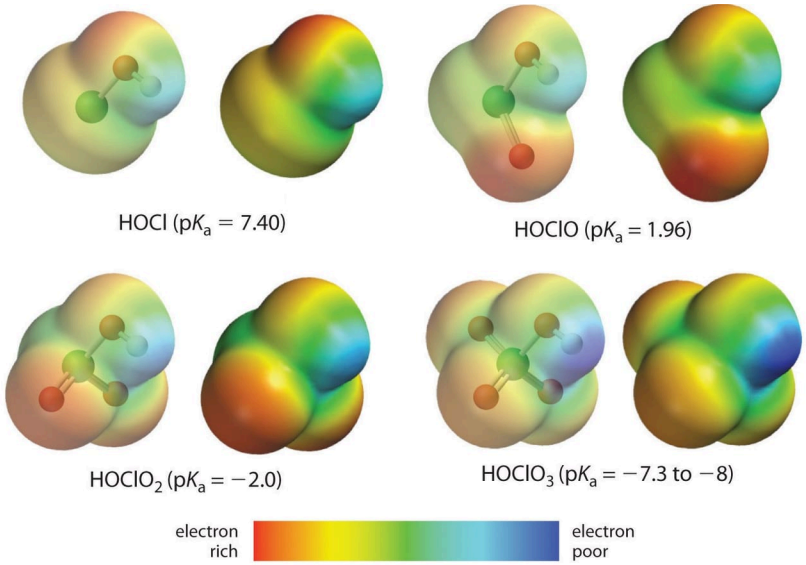


Figure $8.8.2$: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the $\mathrm{O{-}H}$ Unit. These electrostatic potential maps show how the electron density on the $\mathrm{O{-}H}$ unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

Example 8.8.1

Which is the stronger acid in each pair?

a. NH_3 or H_2O

b. H_2S or H_2Te

c. H_3PO_4 or H_3AsO_4

d. $HBrO$ or $HBrO_4$

Solution

a. N and O are in the same row of the periodic table, so the $H{-}N$ and H-O bond strengths are similar. Electronegativity is the more important factor. Since O is more electronegative than N, H_2O is a stronger acid than NH_3.

b. Te is larger than S, so the $H{-}E$ bond strength is the important factor. Since Te is larger, the $H{-}Te$ bond is weaker than the $H{-}S$ bond and H_2Te is a stronger acid than H_2S.

c. Both oxoacids have 4 oxygens, so the important factor is the electronegativity of the central element. P is more electronegative than As, so H_2PO_4 is a stronger acid than H_3AsO_4.

d. In this case, the number of oxygen atoms determines the strength of the acid. Since $HBrO_3$ has more oxygen atoms, it is a stronger acid than $HBrO$.

Summary

Acid strength is closely tied to molecular structure. A weaker $E{-}H$ bond makes it easier for the acid to donate H^+. In addition, a more polar $E{-}H$ bond increases the likelihood of forming an H^+ ion.

For binary acids, HE, two key trends determine acidity. Down a column, acid strength increases as the atomic size of E increases, weakening the $E{-}H$ bond strength. Across a row, acid strength increases as the electronegativity of E increases, increasing the $E{-}H$ bond polarity.

For oxoacids, $O_mE(OH)_n$, acid strength increases with both the number of oxygen atoms and the electronegativity of the central atom, E.

Glossary

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

oxoacid
: A compound containing a nonmetal and one or more hydroxyl groups; also called oxyacid.

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8.9: Lewis Acids and Bases

Learning Objective

- Define Lewis acids as electron pair acceptors and Lewis bases as electron pair donors

In 1923, G. N. Lewis, an American physical chemist, proposed a broader definition of acids and bases:

- A Lewis acid is a substance that can accept a pair of electrons.
- A Lewis base is a substance that can donate a pair of electrons.

In this framework, acid-base reactions involve the transfer of an electron pair from the base to the acid. The donated electron pair is shared between the acid and the base in a covalent bond (Figure $8.9.1$).

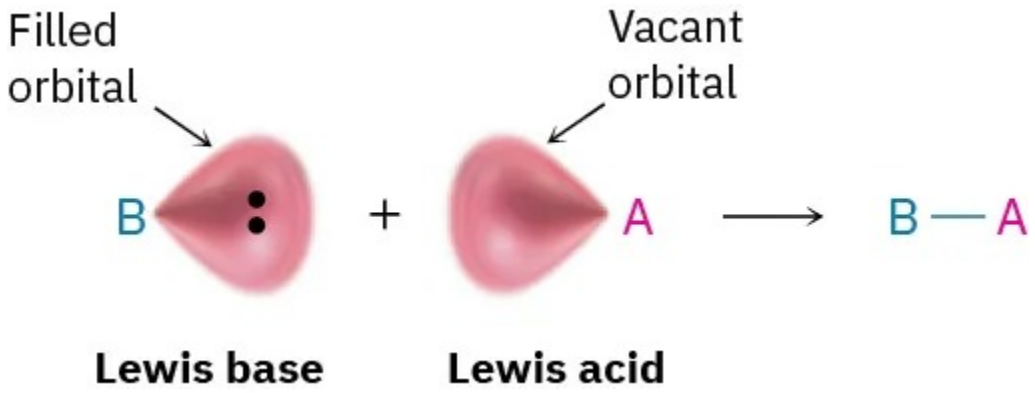
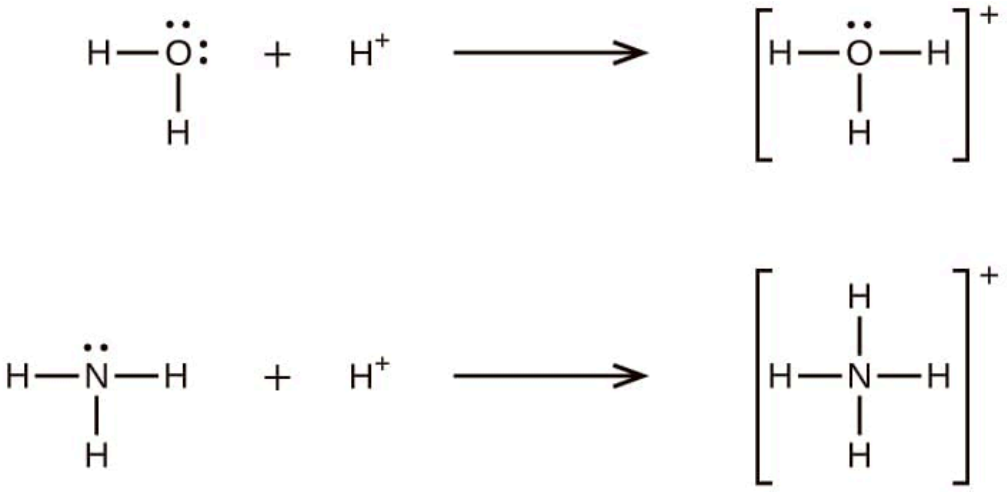


Figure $8.9.1$: A Lewis base (B) has a filled orbital containing a lone pair of electrons, while a Lewis acid (A) has a vacant orbital capable of accepting that pair. When they interact, the electron pair from the base is shared with the acid, forming a covalent bond.

The Lewis definition includes all Brønsted-Lowry acid-base reactions (where $\mathrm{H^+}$ is the acid) as a subset but also applies to many other reactions that do not involve $\mathrm{H^+}$. First, consider two reactions with $\mathrm{H^+}$:

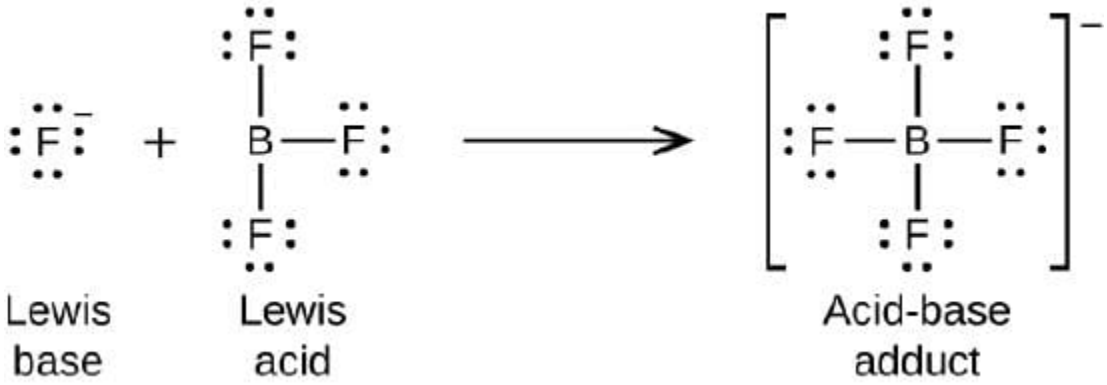
When water reacts with $\mathrm{H^+}$ to form $\mathrm{H_3O^+}$, water donates a lone pair acting as a Lewis base, and $\mathrm{H^+}$ accepts it acting as a Lewis acid.

When ammonia reacts with $\mathrm{H^+}$ to form $\mathrm{NH_4{}^+}$, ammonia donates a lone pair (Lewis base), and $\mathrm{H^+}$ accepts it (Lewis acid).



As the two examples above illustrate, Brønsted-Lowry acid-base reactions represent a subcategory of Lewis acid reactions, specifically, those in which the acid species is H^+.

The next example shows a Lewis acid that is not a Brønsted-Lowry acid. The boron atom in boron trifluoride, BF_3, is a Lewis acid because it has an empty orbital and can accept a lone pair from a Lewis base. In this reaction, a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



This example illustrates how the Lewis definition expands our understanding of acid-base behaviour beyond proton transfer.

Summary

A Lewis acid is a substance that can accept a pair of electrons.

A Lewis base is a substance that can donate a pair of electrons.

The Lewis definition includes Brønsted-Lowry acid-base reactions but also other important reactions in chemistry.

Glossary

Lewis acid
: A substance that can accept a pair of electrons.

Lewis base
: A substance that can donate a pair of electrons.

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8.E: Acid-Base Equilibria (Exercises)

Brønsted-Lowry Acids and Bases

Exercise $8.E.1$*

What is the conjugate base of each of the following?

a. HF

b. $\mathrm{H_2SO_4}$

c. $\mathrm{H_2O}$

d. $\mathrm{HCO_3^-}$

Answer available at the end of this section.

Exercise $8.E.2$*

What is the conjugate acid of each of the following?

a. $\mathrm{OH^-}$

b. $\mathrm{H_2O}$

c. $\mathrm{NH_3}$

d. $\mathrm{HCO_3^-}$

Answer available at the end of this section.

Exercise $8.E.3$*

In each reaction, label the acids, bases, and conjugate acid-base pairs:

a. $\mathrm{HNO_3\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_3^-\,(aq)}$
b. $\mathrm{CN^-\,(aq) + H_2O\,(l) \rightleftharpoons HCN\,(aq) + OH^-\,(aq)}$
c. $\mathrm{H_2SO_4\,(aq) + Cl^-\,(aq) \rightleftharpoons HCl\,(aq) + HSO_4^-\,(aq)}$
d. $\mathrm{HSO_4^-\,(aq) + OH^-\,(aq) \rightleftharpoons SO_4^{2-}\,(aq) + H_2O\,(l)}$
e. $\mathrm{H_2S\,(aq) + NH_2^-\,(aq) \rightleftharpoons HS^-\,(aq) + NH_3\,(aq)}$

Answer available at the end of this section.

Exercise $8.E.4$*

Do the following species represent conjugate acid–base pairs?

a. $\mathrm{H_2O\,(l)}$, $\mathrm{H_3O^+\,(aq)}$

b. $\mathrm{OH^-\,(aq)}$, $\mathrm{H_3O^+\,(aq)}$

c. $NH_3\,(aq)$, $OH^-\,(aq)$

d. $H_2CO_3\,(aq)$, $HCO_3{}^-\,(aq)$

Answer available at the end of this section.

Exercise $8.E.5$*

Calculate the $[OH^-]$ in a solution with $[H_3O^+]$ of 2.8 x 10^{-6} at 25 °C? Is the solution acidic, basic, or neutral? K_w at 25 °C is 1.0 × 10^{-14}

Answer available at the end of this section.

Exercise $8.E.6$**

What is the $[H_3O^+]$ if an aqueous solution has an $[OH^-]$ concentration of 1.6 x 10^{-5} M at 100 °C? Is the solution acidic, basic, or neutral? K_w at 100 °C is 5.6 × 10^{-13}

Answer available at the end of this section.

Exercise $8.E.7$**

Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+]$ = 1.7 × 10^{-7} M.

(K_w is 2.9 × 10^{-14} at 40 °C)

Answer available at the end of this section.

pH and pOH

Exercise $8.E.8$*

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52 at 25 °C? Is the solution acidic, basic, or neutral?

Answer available at the end of this section.

Exercise $8.E.9$*

A calcium hydroxide solution has a $[OH^-]$ of 0.0056 M. Calculate the pH and the pOH of the solution at 25 °C.

Answer available at the end of this section.

Exercise $8.E.10$**

The ionization constant for water (K_w) is 2.90 × 10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

Answer available at the end of this section.

Exercise $8.E.11$**

How many moles of $\mathrm{H_3O^+}$ or $\mathrm{OH^-}$ must be added to adjust the pH of a 1.00 L solution from 7.68 to 8.62? Assume a negligible change in volume with the addition of $\mathrm{H_3O^+}$ or $\mathrm{OH^-}$.

Answer available at the end of this section.

Relative Strengths of Acids and Bases

Exercise $8.E.12$*

Write the reaction for the ionization of HF in water. What is the expression for the ionization constant, K_a?

Answer available at the end of this section.

Exercise $8.E.13$*

Write the reaction for the ionization of $\mathrm{NH_3}$ in water. What is the expression for the ionization constant, K_b?

Answer available at the end of this section.

Exercise $8.E.14$**

Using Figure 7.4.3, determine if K_c is greater than 1 for the following reactions:

a. $\mathrm{H_2CO_3\,(aq) + NO_2^-\,(aq) \rightleftharpoons HCO_3^-\,(aq) + HNO_2\,(aq)}$

b. $\mathrm{H_2CO_3\,(aq) + CN^-\,(aq) \rightleftharpoons HCO_3^-\,(aq) + HCN\,(aq)}$

c. $\mathrm{HF\,(aq) + H_2PO_4^-\,(aq) \rightleftharpoons F^-\,(aq) + H_3PO_4\,(aq)}$

d. $\mathrm{NH_3\,(aq) + HCN\,(aq) \rightleftharpoons NH_4^+\,(aq) + CN^-\,(aq)}$

Answer available at the end of this section.

Exercise $8.E.15$*

The following acids increase in strength as follows:

$\mathrm{HA < HB < HC}$

Which of the conjugate bases $\mathrm{A^-}$, $\mathrm{B^-}$ or $\mathrm{C^-}$ is the strongest base?

Answer available at the end of this section.

Exercise 8.E.16*

What is the ionization constant, K_a, at 25 °C for the weak acid $CH_3NH_3^+$? The ionization constant (K_b) of CH_3NH_2 is 4.4 × 10^{-4}.

Answer available at the end of this section.

Exercise 8.E.17*

Which base is stronger: CH_3NH_2 (K_b = 4.4 x 10^{-4}) or $(CH_3)_2NH$ (K_b = 5.9 x 10^{-4})?
Which conjugate acid is stronger: $CH_3NH_3^+$ or $(CH_3)_2NH_2^+$?

Answer available at the end of this section.

Strong Acids and Bases

Exercise 8.E.18*

Calculate the pH and the pOH of each of the following solutions at 25 °C. Are the solutions acidic, basic, or neutral?

a. 0.000259 M $HClO_4$ b. 0.21 M $NaOH$ c. 0.000071 M $Ba(OH)_2$

Answer available at the end of this section.

Exercise 8.E.19*

What are the $[H_3O^+]$, $[OH^-]$, pH, and pOH of a 0.015 M HNO_3 solution at 25 °C?

Answer available at the end of this section.

Weak Acids and Bases

Exercise 8.E.20*

Acetic acid, CH_3COOH, is the main component in vinegar. List all species present in a 0.1 M solution of acetic acid in order of decreasing concentration.

Answer available at the end of this section.

Exercise 8.E.21*

What is the difference between a weak acid and a strong acid? Does a strong acid always have a lower pH than a weak acid?

Answer available at the end of this section.

Exercise $8.E.22$**

Which solution will have the higher pH?

a. A 0.1 M solution of acetic acid or a 1.0 M solution of acetic acid.

b. A 0.1 M solution of acetic acid or a 0.1 M solution of hydrochloric acid.

c. A 1.0 M solution of an acid with a pK_a of 3.29 or a 1.0 M solution of an acid with a pK_a of 6.32.

Answer available at the end of this section.

Exercise $8.E.23$*

A solution of $\mathrm{HNO_2}$ contains 0.52 M $\mathrm{HNO_2}$, 0.014 M $\mathrm{NO_2^-}$, and 0.014 M $\mathrm{H_3O^+}$ at equilibrium. What is the expression and value for the ionization constant, K_a?

Answer available at the end of this section.

Exercise $8.E.24$*

A solution of trimethylamine contains 0.25 M $\mathrm{(CH_3)_3N}$ and 4.3×10^{-3} M of $\mathrm{OH^-}$ and $\mathrm{(CH_3)_3NH^+}$. What is the expression and value for the ionization constant, K_b?

Answer available at the end of this section.

Exercise $8.E.25$**

The pH of a 0.15 M solution of $\mathrm{HSO_4^-}$ is 1.43. Determine K_a for $\mathrm{HSO_4^-}$.

Answer available at the end of this section.

Exercise $8.E.26$**

The pH of a solution of household ammonia, a 0.950 M solution of $\mathrm{NH_3}$, is 11.612. Determine K_b for $\mathrm{NH_3}$.

Answer available at the end of this section.

Exercise $8.E.27$**

Calculate the concentration of the species present at equilibrium and the pH of a 0.0092 M solution of HClO at 25 °C. K_a = 2.9×10^{-8}

Answer available at the end of this section.

Exercise $8.E.28$**

Calculate the concentration of the species present at equilibrium and the pH of a 0.0784 M solution of $\mathrm{C_6H_5NH_2}$ at 25 °C. K_b = 4.6×10^{-10}

Answer available at the end of this section.

Exercise $8.E.29$**

Calculate the pH and the percent ionization of $\mathrm{HNO_2}$ (K_a = 4.5 x 10^{-4}) in

a) 1.0 M $\mathrm{HNO_2}$ b) 0.25 M $\mathrm{HNO_2}$

Answer available at the end of this section.

Exercise $8.E.30$**

What is the pH of a 0.081 M solution of HCN? K_a = 6.2 x 10^{-10}

Answer available at the end of this section.

Exercise $8.E.31$**

Propionic acid, $\mathrm{C_2H_5CO_2H}$ (K_a = 1.34 x 10^{-5}), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698 M solution of $\mathrm{C_2H_5CO_2H}$?

Answer available at the end of this section.

Acid-Base Properties of Salt Solutions

Exercise $8.E.32$*

Explain with equations whether an aqueous solution of these salts is acidic, basic, or neutral.

a. $\mathrm{K_2CO_3}$ b. $\mathrm{NH_4Br}$ c. $\mathrm{KClO_4}$

Answer available at the end of this section.

Exercise $8.E.33$**

Order the 0.10 M aqueous solutions of the following salts in terms of increasing pH:

$\mathrm{Na_2CO_3(aq)}$, $\mathrm{NaCl(aq)}$, $\mathrm{NaHCO_3(aq)}$, $\mathrm{NH_4Cl(aq)}$

For $\mathrm{H_2CO_3}$, K_{a1} = 4.5 x 10^{-7} and K_{a2} = 4.7 x 10^{-11}

Answer available at the end of this section.

Exercise $8.E.34$**

Is an aqueous solution of $\mathrm{NH_4NO_2}$ acidic, basic, or neutral? (For $\mathrm{NH_3}$: K_b = 1.8 x 10^{-5}; For $\mathrm{HNO_2}$: K_a = 7.1 x 10^{-4})

Answer available at the end of this section.

Exercise $8.E.35$***

What is the pH of 0.15 M NaF? K_a of HF is 6.8 x 10^{-4}

Answer available at the end of this section.

Exercise $8.E.36$***

What is the pH of 0.25 M $\mathrm{NH_4Br}$? (For $\mathrm{NH_3}$: K_b = 1.8 x 10^{-5})

Answer available at the end of this section.

Molecular Structure

Exercise $8.E.37$*

Which is the stronger acid in each pair?

a. HI or HF

b. $\mathrm{PH_3}$ or HCl

c. $\mathrm{H_2O}$ or HF

d. $\mathrm{H_2S}$ or HBr

Answer available at the end of this section.

Exercise $8.E.38$*

Which is the stronger acid in the pair?

a. $\mathrm{HClO_2}$ or HClO

b. $\mathrm{HClO_4}$ or $\mathrm{H_2SO_4}$

c. $\mathrm{HClO_3}$ or $\mathrm{HBrO_3}$

Answer available at the end of this section.

Exercise $8.E.39$**

Place the following acids in order of increasing acid strength:

$\mathrm{HIO_3}$, $\mathrm{HClO_4}$, HIO, $\mathrm{HIO_4}$

Answer available at the end of this section.

Additional Problems

Exercise $8.E.40$**

Arrange these acids in order of increasing strength.

- acid A: pK_a = 1.52
- acid B: pK_a = 6.93
- acid C: pK_a = 3.86

Given solutions with the same initial concentration of each acid, which would have the highest pH?

Answer available at the end of this section.

Exercise $8.E.41$***

White vinegar is a 5.0% by mass solution of acetic acid, $\mathrm{CH_3COOH}$, in water (i.e. 5.0 g of acetic acid/100 g of solution). If the density of solution is 1.007 g/cm^3, what is the pH? K_a = 1.8 x 10^{-5}.

Answer available at the end of this section.

Exercise $8.E.42$**

Arrange the following ions in increasing basicity:

$\mathrm{BrO_2^-}$, $\mathrm{ClO_2^-}$, $\mathrm{IO_2^-}$,

Answer available at the end of this section.

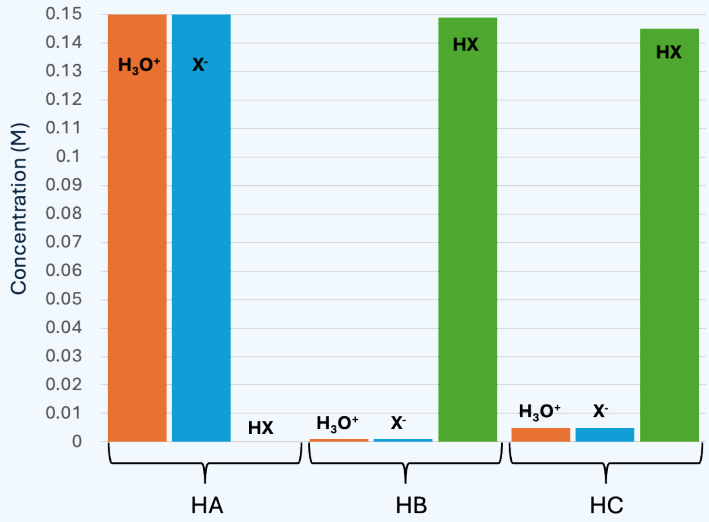
Exercise $8.E.43$***

What is the pH of 0.010 M $\mathrm{HClO_2}$ (K_a = 1.1 x 10^{-2})? What is the percent ionization?

Answer available at the end of this section.

Exercise $8.E.44$**

The bar graph below shows the equilibrium concentrations of $\mathrm{H_3O^+}$, $\mathrm{X^-}$, and HX of three different acid solutions, HA, HB and HC all with the same initial concentration, 0.15 M.



a. Which of the acids are weak acids? Place the acids in terms of increasing ionization constant, K_a.

b. Would a solution of NaA (where $\mathrm{A^-}$ is the conjugate acid of HA be acidic, basic, or neutral?

c. Which is the stronger base, $\mathrm{B^-}$ or $\mathrm{C^-}$?

Answer available at the end of this section.

Exercise $8.E.45$***

Procaine (K_b = 7.0 x 10^{-6}) is a local anesthetic that forms a salt with HCl. What is the pH of a 0.073 M of the salt, known as novocaine?

Answer available at the end of this section.

Exercise $8.E.46$**

A 70 kg (154 lb) adult has a blood volume of 5.2 L and a blood pH of 7.42. How many hydronium ions ($\mathrm{H_3O^+}$) are present in the adult's blood?

Answer available at the end of this section.

Exercise $8.E.47$**

A 0.57 M solution of a weak acid, HA, is 2.4% ionized. What is the K_a of the acid?

Answer available at the end of this section.

Answers

Exercise $8.E.1$*

To find the conjugate base, remove a proton ($\mathrm{H^+}$) from each acid:

a. $\mathrm{F^-}$

b. $\mathrm{HSO_4^-}$

c. OH^-

d. $CO_3{}^{2-}$

Exercise $8.E.2$*

To find the conjugate acid, add a proton to each base:

a. H_2O

b. H_3O^+

c. $NH_4{}^+$

d. H_2CO_3

Exercise $8.E.3$*

a. The acids are HNO_3 and H_3O^+. The bases are H_2O and $NO_3{}^-$. The conjugate acid-base pairs are HNO_3 and $NO_3{}^-$, and H_3O^+ and H_2O.

b. The acids are H_2O and HCN. The bases are OH^- and CN^-. The conjugate acid-base pairs are H_2O and OH^-, and HCN and CN^-.

c. The acids are H_2SO_4 and HCl. The bases are $HSO_4{}^-$ and Cl^-. The conjugate acid-base pairs are H_2SO_4 and $HSO_4{}^-$, and HCl and Cl^-.

d. The acids are $HSO_4{}^-$ and H_2O. The bases are $SO_4{}^{2-}$ and OH^-. The conjugate acid-base pairs are $HSO_4{}^-$ and $SO_4{}^{2-}$, and H_2O and OH^-.

e. The acids are H_2S and NH_3. The bases are HS^- and $NH_2{}^-$. The conjugate acid-base pairs are H_2S and HS^-, and NH_3 and $NH_2{}^-$.

Exercise $8.E.4$*

a. Yes, H_2O is the base and H_3O^+ is the conjugate acid.

b. No.

c. No.

d. Yes, H_2CO_3 is the acid and $HCO_3{}^-$ is the conjugate base.

Exercise $8.E.5$*

$$K_w = [OH^-][H_3O^+]$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = 3.6 \times 10^{-9}\ \text{M}$$

Acidic because $[H_3O^+] > [OH^-]$

Exercise $8.E.6$**

$$K_w = [OH^-][H_3O^+]$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = 3.5 \times 10^{-8}\ \text{M}$$

Basic because $[H_3O^+] < [OH^-]$

Exercise $8.E.7$**

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C:

$K_w = [OH^-][H_3O^+] = x^2 = 2.9 \times 10^{-14}$

$x = [OH^-] = [H_3O^+] = \sqrt{2.9 \times 10^{-14}} = 1.7 \times 10^{-7}$

Exercise $8.E.8$*

$$\text{pH} = -\log[H_3O^+] \quad [H_3O^+] = 10^{-8} = 3.0 \times 10^{-7}\ \text{M}$$

$$\text{pOH} = 14 - \text{pH} = 7.48 \quad [OH^-] = 10^{-\text{pOH}} = 3.3 \times 10^{-8}\ \text{M}$$

Acidic because $[H_3O^+] > [OH^-]$

Note: Because there are two decimal places in the pH, there are two significant figures in the concentration.

Exercise $8.E.9$*

$$\text{pOH} = -\log[OH^-] = 2.25$$

$$\text{pH} = 14 - \text{pOH} = 11.75$$

Note: there are two decimal places in the pH and pOH because there are two significant figures in the concentration.

Exercise $8.E.10$**

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C,

$$K_w = [OH^-][H_3O^+] = x^2 = 2.90 \times 10^{-14}$$

$$x = [OH^-] = [H_3O^+] = \sqrt{2.90 \times 10^{-14}} = 1.70 \times 10^{-7}$$

$$\text{pH} = -\log(1.70 \times 10^{-7}) = -(-6.77) = 6.770$$

$$\text{pOH} = -\log(1.70 \times 10^{-7}) = 6.770$$

Note: there are three decimal places in the pH and pOH because there are three significant figures in the concentration.

Exercise $8.E.11$**

The pH of the solution is increasing or becoming more basic, so OH^- must be added. Since pOH is a measure of $[OH^-]$, let's work in pOH.

Initial

$$\text{pOH} = 14 - 7.68 = 6.32 \quad [OH^-] = 10^{-\text{pOH}} = 4.79 \times 10^{-7}\ \text{M}$$

$$\text{moles } OH^- = 4.79 \times 10^{-7}\ \text{mol/L} \times 1.00\ \text{L} = 4.79 \times 10^{-7}\ \text{mol}$$

Final

$$\text{pOH} = 14 - 8.62 = 5.38 \quad [OH^-] = 10^{-\text{pOH}} = 4.17 \times 10^{-6}\ \text{M}$$

$$\text{moles } OH^- = 4.17 \times 10^{-6} \text{ mol/L} \times 1.00 \text{ L} = 4.17 \times 10^{-6} \text{ mol}$$

The amount of OH^- added is the difference in the number of moles in the solutions:

$$4.17 \times 10^{-6} \text{ mol} - 4.79 \times 10^{-7} \text{ mol} = 3.7 \times 10^{-6} \text{ mol}$$

Exercise $8.E.12$*

$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$

$K_a = \frac{[F^-][H_3O^+]}{[HF]}$

Exercise $8.E.13$*

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq)$

$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]}$

Exercise $8.E.14$**

To determine the equilibrium position, we need to look at the relative strength of the acids and bases in the reactants and products.

a. The acid in the forward reaction is H_2CO_3, and in the reverse direction it is HNO_2. From Figure 7.4.3, we see that HNO_2 is the stronger acid (this also means that $HCO_3{}^-$ is a stronger base than $NO_2{}^-$), so the reverse reaction, from stronger acid and stronger base to weaker acid and base, would occur to a greater extent than the forward reaction. Therefore, K_c is less than 1.

b. The acid in the forward reaction is H_2CO_3, and in the reverse direction it is HCN. From Figure 7.4.3, we see that H_2CO_3 is the stronger acid (this also means that CN^- is a stronger base than $HCO_3{}^-$), so the forward reaction, from stronger acid and stronger base to weaker acid and base, would occur to a greater extent than the reverse reaction. Therefore, K_c is greater than 1.

c. The acid in the forward reaction is HF, and in the reverse direction it is H_3PO_4. From Figure 7.4.3, we see that H_3PO_4 is the stronger acid (this also means that F^- is a stronger base than $H_2PO_4{}^-$), so the reverse reaction, from stronger acid and stronger base to weaker acid and base, would occur to a greater extent than the forward reaction. Therefore, K_c is less than 1.

d. The acid in the forward reaction is HCN, and in the reverse direction it is $NH_4{}^+$. From Figure 7.4.3, we see that $NH_4{}^+$ is the stronger acid (this also means that CN^- is a stronger base than NH_3), so the reverse reaction, from stronger acid and stronger base to weaker acid and base, would occur to a greater extent than the forward reaction. Therefore, K_c is less than 1.

Exercise $8.E.15$*

The strength of an acid and its conjugate base are inversely related—the stronger the acid, the weaker its conjugate base. Since HC is the strongest acid, C^- is the weakest of the bases. HA, the weakest acid, has the strongest conjugate base, A^-.

Exercise $8.E.16$*

For a conjugate acid-base pair,

$K_a \times K_b = K_w$

$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11}$

Exercise $8.E.17$*

The stronger base is the one with the larger K_b value. Since $(CH_3)_2NH$ has larger value, it is the stronger base. The strength of a base and its conjugate acid are inversely proportional, so $CH_3NH_3{}^+$ is the stronger acid.

Exercise $8.E.18$*

a. $HClO_4$ is a strong acid, so it ionizes completely in water:

$HClO_4(aq) + H_2O(l) \rightarrow ClO_4{}^-(aq) + H_3O^+(aq)$

Since $HClO_4$ dissociated fully, the concentration of H_3O^+ equals the initial concentration of the acid:

$[H_3O^+] = 0.000259 \text{ M}$

$\text{pH} = -\log[H_3O^+] = 3.587; \text{ pOH} = 14 - \text{pH} = 10.413$

Acidic

b. $NaOH$ is a strong base, so the $[OH^-]$ = 0.21 M

$\text{pOH} = -\log[OH^-] = 0.68; \text{ pH} = 14 - \text{pOH} = 13.32$

Basic

c. For each mole of $Ba(OH)_2$, two moles of OH^- are formed.

$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$

$[OH^-] = 2\,(0.000071 \text{ M}) = 0.00014 \text{ M}; \text{ pOH} = -\log[OH^-] = 3.85; \text{ pH} = 14 - \text{pOH} = 10.15$

Basic

Exercise $8.E.19$*

HNO_3 is a strong acid, so it ionizes completely in water:

$HNO_3(aq) + H_2O(l) \rightarrow NO_3{}^-(aq) + H_3O^+(aq)$

Therefore $[H_3O^+] = 0.015 \text{ M}$. $\text{pH} = -\log[H_3O^+] = 1.82; \text{ pOH} = 14 - \text{pH} = 12.18$

$[OH^-] = 10^{-\text{pOH}} = 6.7 \times 10^{-13} \text{ M}$

Exercise $8.E.20$*

Acetic acid is a weak acid, so it only ionizes slightly in water:

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

Water is present in the greatest amount. After water, the unreacted CH_3COOH has the greatest concentration. $[CH_3COO^-]$ and $[H_3O^+]$ are equal due to the 1:1 mole ratio in the ionization reaction. A small amount of $[OH^-]$ is present due to the autoionization of water.

$[H_2O] > [CH_3COOH] > [CH_3COO^-] \approx [H_3O^+] > [OH^-]$

Exercise $8.E.21$*

A strong acid fully ionizes in water, meaning nearly all acid molecules react to form H_3O^+ ions and the conjugate base (K_a is very large). A weak acid only partially

ionizes in water, so a significant amount of the acid remains unreacted in solution. ($K_a << 1$).

The pH of a solution depends on both the concentration of the acid and the completeness of its ionization. While a strong acid has a lower pH than a weak acid at the same concentration, a dilute strong acid could have a higher pH than a more concentrated weak acid. The concentration of the acid is critical in determining the actual pH.

Exercise $8.E.22$**

a. Both solutions contain the same acid but at different concentrations.

0.1 M acetic acid: Lower concentration → Fewer protons released → Higher pH.

1.0 M acetic acid: Higher concentration → More protons released → Lower pH.

b. Both solutions have the same concentration (0.1 M), but the acids have different strengths. Acetic acid is a weak acid, so it partially ionizes in water. Hydrochloric acid is a strong acid, so it ionizes fully in water and produces more H_3O^+. Therefore, 0.1 M acetic acid (weak acid) will have a higher pH compared to the strong acid HCl at the same concentration.

c. In both solutions, the concentration is the same (1.0 M), but the acids differ in strength. The acid with the lower pK_a is the stronger acid, which will produce more H_3O^+ and have a lower pH. The acid with a pK_a of 6.32 will have a higher pH.

Exercise $8.E.23$*

$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons NO_2^-\,(aq) + H_3O^+\,(aq)$

$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(0.014)(0.014)}{(0.52)} = 3.8 \times 10^{-4}$

Exercise $8.E.24$*

$(CH_3)_3N\,(aq) + H_2O\,(l) \rightleftharpoons (CH_3)_3NH^+\,(aq) + OH^-\,(aq)$

$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(4.3\times10^{-3})(4.3\times10^{-3})}{(0.25)} = 7.4 \times 10^{-5}$

Exercise $8.E.25$**

To find K_a, we need the equilibrium concentrations of the species:

	$HSO_4^-\,(aq)$ +	$H_2O\,(l)$ ⇌	$SO_4^{2-}\,(aq)$ +	$H_3O^+\,(aq)$
Initial	0.15 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.15 - x		x	x

We can find the equilibrium $[H_3O^+]$ and therefore x from the pH.

$[H_3O^+] = 10^{-pH} = 10^{-1.43} = 0.037\ M = x$

$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(0.037)(0.037)}{(0.15-0.037)} = 1.2 \times 10^{-2}$

Exercise $8.E.26$**

	$NH_3\,(aq)$ +	$H_2O\,(l)$ ⇌	$NH_4^+\,(aq)$ +	$OH^-\,(aq)$
Initial	0.950 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.950 - x		x	x

$[OH^-] = 10^{-pOH}$; $pOH = 14 - pH = 2.388$; $[OH^-] = 10^{-pOH} = 10^{-2.388} = 0.00409\ M = x$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.00409)(0.00409)}{(0.950-0.00409)} = 1.77 \times 10^{-5}$

Exercise $8.E.27$**

	$HClO\,(aq)$ +	$H_2O\,(l)$ ⇌	$ClO^-\,(aq)$ +	$H_3O^+\,(aq)$
Initial	0.0092 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0092 - x		x	x

$K_a = \frac{[ClO^-][H_3O^+]}{[HClO]} = \frac{x^2}{0.0092-x} = 2.9 \times 10^{-8}$

Since K_a is very small, the acid will only ionize slightly, and we can assume that $x << 0.0092\ M$.

$K_a = \frac{x^2}{0.0092} = 2.9 \times 10^{-8}\ x = 1.6 \times 10^{-5} M$

Checking assumption:

$\frac{1.6\times10^{-5}}{0.0092} \times 100\% = 0.17\%$

The assumption is valid since the percentage is less than 5%.

$[H_3O^+] = [ClO^-] = x = 1.6 \times 10^{-5}\ M$; $[HClO] = 0.0092 - x = 0.0092 - 1.6 \times 10^{-5} = 0.0092\ M$

$pH = -\log[H_3O^+] = 4.79$

A small amount of OH^- is present due to the autoionization of water:

$[OH^-] = \frac{K_w}{[H_3O^+]} = 6.3 \times 10^{-10}\ M$

Exercise $8.E.28$**

	$C_6H_5NH_2\,(aq)+$	$H_2O\,(l)$ ⇌	$C_6H_5NH_3^+\,(aq)+$	$OH^-\,(aq)$
Initial	0.0784 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0784 - x		x	x

$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{x^2}{(0.0784-x)} = 4.6 \times 10^{-10}$

Since K_b is very small, the base will only ionize slightly and we can assume that \(\mathrm{x << 0.0784 ~M}\).

$K_b = \frac{x^2}{(0.0784)} = 4.6 \times 10^{-10}\ x = 6.01 \times 10^{-6} M$

Checking assumption:

$\frac{6.01\times10^{-6}}{0.0784} \times 100\% = 0.00766\%$

The assumption is valid since the percentage is less than 5%.

$[OH^-] = [C_6H_5NH_3^+] = x = 6.01 \times 10^{-6}\ \text{M}; \quad [C_6H_5NH_2] = 0.0784 - x = 0.0784 - 6.01 \times 10^{-6} = 0.0784\ \text{M}$

$\text{pOH} = -\log[OH^-] = 5.221; \quad \text{pH} = 14 - \text{pOH} = 8.779$

$[H_3O^+] = 10^{-\text{pH}} = 1.66 \times 10^{-9}\ \text{M}$

Exercise $8.E.29$**

a)

	$HNO_2\,(aq)+$	$H_2O\,(l)$ ⇌	$NO_2^-\,(aq)+$	$H_3O^+\,(aq)$
Initial	1.0 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	1.0 M - x		x	x

$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{x^2}{1.0-x} = 4.5 \times 10^{-4}$

Since K_a is small, the acid will only ionize slightly, and we can assume that $\text{x} << 1.0\ \text{M}$.

$K_a = \frac{x^2}{1.0} = 4.5 \times 10^{-4}\ x = 0.021 M$

Checking assumption:

$\frac{0.021}{1.0} \times 100\% = 2.1\%$

The assumption is valid since the percentage is less than 5%.

$\text{pH} = -\log[H_3O^+] = 1.67$

$$\%\ \text{ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% = \frac{0.021\ M}{1.0\ M} \times 100\% = 2.1\%$$

b)

	$HNO_2\,(aq)+$	$H_2O\,(l)$ ⇌	$NO_2^-\,(aq)+$	$H_3O^+\,(aq)$
Initial	0.25 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.25 M - x		x	x

$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{x^2}{0.25-x} = 4.5 \times 10^{-4}$

Since K_a is small, the acid will only ionize slightly, and we can assume that $\text{x} << 0.25\ \text{M}$.

$K_a = \frac{x^2}{0.25} = 4.5 \times 10^{-4}\ x = 0.011 M$

Checking assumption:

$\frac{0.011}{0.25} \times 100\% = 4.2\%$

The assumption is valid since the percentage is less than 5%.

$pH = -\log[H_3O^+] = 1.97$

$$\%\ \text{ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% = \frac{0.011\ M}{0.25\ M} \times 100\% = 4.2\%$$

Exercise $8.E.30$**

	$HCN\,(aq)+$	$H_2O\,(l)$ ⇌	$CN^-\,(aq)+$	$H_3O^+\,(aq)$
Initial	0.081 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.081 - x		x	x

$K_a = \frac{[CN^-][H_3O^+]}{[HCN]} = \frac{x^2}{0.081-x} = 6.2 \times 10^{-10}$

Since K_a is very small, the acid will only ionize slightly and we can assume that $\text{x} << 0.081\ \text{M}$.

$K_a = \frac{x^2}{0.081} = 6.2 \times 10^{-10}\ x = 7.1 \times 10^{-6} M$

Checking assumption:

$\frac{7.1\times10^{-6}}{0.081}\times100\%=0.0087\%$

The assumption is valid since the percentage is less than 5%.

$[H_3O^+]=x=7.1\times10^{-6}\ M$

$pH=-\log[H_3O^+]=5.15$

Exercise $8.E.31$**

	$C_2H_5CO_2H\,(aq)+$	$H_2O\,(l)$ ⇌	$C_2H_5CO_2^-\,(aq)+$	$H_3O^+\,(aq)$
Initial	0.698 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.698 - x		x	x

$K_a=\frac{[C_2H_5CO_2^-][H_3O^+]}{[C_2H_5CO_2H]}=\frac{x^2}{0.698-x}=1.34\times10^{-5}$

Since K_a is very small, the acid will only ionize slightly and we can assume that $x << 0.698\ M$.

$K_a=\frac{x^2}{0.698}=1.34\times10^{-5}\ x=3.06\times10^{-3}M$

Checking assumption:

$\frac{3.06\times10^{-3}}{0.698}\times100\%=0.438\%$

The assumption is valid since the percentage is less than 5%.

$[H_3O^+]=x=3.06\times10^{-3}\ M$

$pH=-\log[H_3O^+]=2.514$

Exercise $8.E.32$*

a. Dissociation in water:

$K_2CO_3\ \rightarrow 2\,K^+\,(aq)+{CO_3}^{2-}\,(aq)$

K^+ does not react with water to form either H_3O^+ or OH^-, so it gives a neutral solution.

${CO_3}^{2-}$ is the conjugate base of a weak acid, so it can act as a base in water:

${CO_3}^{2-}+H_2O\,(l)\ \rightleftharpoons {HCO_3}^-\,(aq)+OH^-\,(aq)$

Since OH^- is formed in solution, the solution is basic.

b. $NH_4Br\ \rightarrow {NH_4}^+\,(aq)+Br^-\,(aq)$

${NH_4}^+$ is the conjugate acid of NH_3, a weak base, and can donate a proton to water:

${NH_4}^+\,(aq)+H_2O\,(l)\ \rightleftharpoons NH_3\,(aq)+H_3O^+\,(aq)$

Since H_3O^+ is formed the solution is acidic.

The Br^- ion is the conjugate base of a strong acid (HBr), so it is such a weak base that its base strength can be considered negligible and does not affect the pH of the solution.

c. $KClO_4\ \rightarrow K^+\,(aq)+{ClO_4}^-\,(aq)$

K^+ does not react with water to form either H_3O^+ or OH^-, so it gives a neutral solution.

The ${ClO_4}^-$ ion is the conjugate base of a strong acid ($HClO_4$), so it is such a weak base that its base strength can be considered negligible.

The solution is neutral since neither ion affects the pH of the solution.

Exercise $8.E.33$**

For each salt, consider the ions present when the salt dissolves.

a. $Na_2CO_3\ \rightarrow 2\,Na^+\,(aq)+{CO_3}^{2-}\,(aq)$

Na^+ does not react with water to form either H_3O^+ or OH^-, so it gives a neutral solution.

${CO_3}^{2-}$ is the conjugate base of the weak acid ${HCO_3}^-$. Therefore, ${CO_3}^{2-}$ can act as a base in water:

${CO_3}^{2-}+H_2O\,(l)\ \rightleftharpoons {HCO_3}^-\,(aq)+OH^-\,(aq)$

Because ${CO_3}^{2-}$ produces OH^- in solution, the solution is basic.

b. $NaCl\ \rightarrow Na^+\,(aq)+Cl^-\,(aq)$

Na^+ does not react with water to form either H_3O^+ or OH^-, so it gives a neutral solution. The Cl^- ion is the conjugate base of a strong acid (HCl), so it is such a weak base that its base strength can be considered negligible and does not affect the pH of the solution. The solution is neutral.

c. $NaHCO_3\ \rightarrow Na^+\,(aq)+{HCO_3}^-\,(aq)$

Na^+ does not react with water to form either H_3O^+ or OH^-, so it gives a neutral solution.

${HCO_3}^-$ is amphiprotic, meaning it can act as both an acid and a base:

${HCO_3}^-\,(aq)+H_2O\,(l)\ \rightleftharpoons {H_2CO_3}^-\,(aq)+OH^-\,(aq)\ \ K_b=\frac{K_w}{K_{a1}}=2.2\times10^{-8}$

${HCO_3}^-\,(aq)+H_2O\,(l)\ \rightleftharpoons {CO_3}^{2-}\,(aq)+H_3O^+\,(aq)\ \ K_a=K_{a2}=4.7\times10^{-11}$

Since $K_b > K_a$, the solution is basic. However, ${HCO_3}^-$ is a weaker base than ${CO_3}^{2-}$, so the pH of the Na_2CO_3 solution would be higher than that of a $NaHCO_3$ solution.

d. $NH_4Cl\ \rightarrow {NH_4}^+\,(aq)+Cl^-\,(aq)$

${NH_4}^+$ is the conjugate acid of the weak base NH_3. Hence, ${NH_4}^+$ can donate a proton to water:

${NH_4}^+\,(aq)+H_2O\,(l)\ \rightleftharpoons NH_3\,(aq)+H_3O^+\,(aq)$

Since H_3O^+ is formed the solution is acidic.

The Cl^- ion is the conjugate base of a strong acid (HCl), so it is such a weak base that its base strength can be considered negligible and does not affect the pH of the solution.

Since we are ordering the solutions in terms of increasing pH, we are going from most acidic to most basic:

$NH_4Cl(aq) < NaCl(aq) < NaHCO_3(aq) < Na_2CO_3(aq)$

Exercise $8.E.34$**

$NH_4Cl \rightarrow NH_4^+(aq) + NO_2^-(aq)$

NH_4^+ is the conjugate acid of the weak base NH_3. Hence, NH_4^+ can donate a proton to water:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

NO_2^- is the conjugate base of the weak acid HNO_2. Therefore, NO_2^- can act as a Brønsted-Lowry base in water:

$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$

The pH of the solution depends on the relative strengths of the acid (NH_4^+) and the base (NO_2^-). To determine whether the solution is acidic or basic, we compare their ionization constants.

$K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$

$K_b(NO_2^-) = \frac{K_w}{K_a(HNO_2)} = \frac{1.0\times10^{-14}}{7.1\times10^{-4}} = 1.4\times10^{-11}$

Since $K_a > K_b$ more H_3O^+ will form than OH^-, so the solution will be acidic.

Exercise $8.E.35$***

	$F^-(aq)$ +	$H_2O(l)$ ⇌		$HF(aq)$ +	$OH^-(aq)$
Initial	0.15 M		X	0 M	0 M
Change	- x			+ x	+ x
Equilibrium	0.15 - x			x	x

$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{x^2}{(0.15-x)} = \frac{K_w}{K_a(HF)} = 1.5\times10^{-11}$

Since K_b is very small, the base will only ionize slightly and we can assume that $x << 0.698$ M.

$K_b = \frac{x^2}{(0.15)} = 1.5\times10^{-11}\ x = 1.5\times10^{-6} M$

Checking assumption:

$\frac{1.5\times10^{-6}}{0.15}\times100\% = 0.001\%$

The assumption is valid since the percentage is less than 5%.

$[OH^-] = x = 1.5\times10^{-6}$ M

$pOH = -\log[OH^-] = 5.82$

$pH = 14 - pOH = 8.18$

Exercise $8.E.36$***

	$NH_4^+(aq)$ +	$H_2O(l)$ ⇌		$NH_3(aq)$ +	$H_3O^+(aq)$
Initial	0.25 M		X	0 M	0 M
Change	- x			+ x	+ x
Equilibrium	0.25 - x			x	x

$K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$

$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{0.25-x} = 5.6\times10^{-10}$

Since K_a is very small, the acid will only ionize slightly and we can assume that $x << 0.25$ M.

$K_a = \frac{x^2}{0.25} = 5.6\times10^{-10}\ x = 1.2\times10^{-5} M$

Checking assumption:

$\frac{1.2\times10^{-5}}{0.25}\times100\% = 0.0047\%$

The assumption is valid since the percentage is less than 5%.

$[H_3O^+] = x = 1.2\times10^{-5}$ M

$pH = -\log[H_3O^+] = 4.93$

Video solution

Exercise $8.E.37$*

The strength of an $H-X$ acid depends on two key factors:

1. Bond strength of $H-X$
   - A weaker bond means the hydrogen ion (H^+) is more easily released, making the acid stronger.
   - Bond strength decreases down a group in the periodic table as atom size increases.
2. Electronegativity of X
   - A more electronegative atom pulls electron density away from hydrogen, increasing bond polarity and making it easier for a base (like water) to remove H^+.
   - For acids in the same row, higher electronegativity leads to stronger acidity.
   - For acids in the same group, bond strength is the dominant factor.

a. In comparing HI and HF, bond strength dominates because iodine and fluorine are in the same group. The much larger iodine atom forms a weaker $H-I$ bond than the smaller fluorine does in $H-F$. The weaker $H-I$ bond more readily releases H^+, so HI is stronger than HF.

b. When considering PH_3 and HCl, electronegativity is key because phosphorus and chlorine are in the same row. Chlorine is significantly more electronegative, creating a strongly polarized $H-Cl$ bond that more readily loses H^+. Consequently, HCl is stronger than PH_3.

c. For HF and H_2O, electronegativity is again the important factor since O and F are in the same row. F is more electronegative than O, so the $H-F$ bond is more

polar than the $\mathrm{H-O}$, making it easier for a water molecule to pull $\mathrm{H^+}$ away. Therefore HF is stronger than $\mathrm{H_2O}$.

d. In comparing HBr and $\mathrm{H_2S}$, bond strength is the key factor. Although Br is slightly more electronegative than S, both atoms are in different groups and different periods, so bond strength dominates. The $\mathrm{H-Br}$ bond is significantly weaker than the $\mathrm{H-S}$ bond due to the larger atomic radius of Br. This makes it easier for HBr to donate a proton. HBr is the stronger acid.

Exercise $8.E.38$**

In comparing oxoacids, the acidic hydrogen is bonded to an oxygen atom in all cases, so $\mathrm{H-X}$ bond strength is not a factor. Instead, two key factors determine the acid strength of oxoacids:

1. Electronegativity of the central atom

A more electronegative central atom withdraws electron density from the $\mathrm{O-H}$ bond, increasing its polarity and making it easier to lose $\mathrm{O-H^+}$.

2. Number of oxygen atoms
More oxygen atoms around the central atom pull additional electron density from the $\mathrm{O-H}$ bond, increasing acid strength.

a. $\mathrm{HClO_2}$ is a stronger acid than HClO because the central atom is the same (Cl) and $\mathrm{HClO_2}$ has an additional O atom, which makes the $\mathrm{O-H}$ more polar and more easily ionized.

b. $\mathrm{HClO_4}$ is a stronger acid than $\mathrm{H_2SO_4}$ because Cl is more electronegative than S, which makes the $\mathrm{O-H}$ bond more polar and more easily ionized.

c. $\mathrm{HClO_3}$ is a stronger acid than $\mathrm{HBrO_3}$ because Cl is more electronegative than Br, which makes the $\mathrm{O-H}$ bond more polar and more easily ionized.

Exercise $8.E.39$**

Two key factors determine the acid strength of oxoacids:

1. Electronegativity of the central atom

A more electronegative central atom withdraws electron density from the $\mathrm{O-H}$ bond, increasing its polarity and making it easier to lose $\mathrm{H^+}$.

2. Number of oxygen atoms
More oxygen atoms around the central atom means additional electron withdrawal, which further polarizes the $\mathrm{O-H}$ bond and increases acid strength.

HIO has the fewest O atoms and I is less negative than Cl, so HIO is the weakest of the acids.

$\mathrm{HIO} < \mathrm{HIO_3} < \mathrm{HIO_4} < \mathrm{HClO_4}$

Exercise $8.E.40$**

The lower the pK_a, the stronger the acid. Therefore, the order of increasing acid strength is:

$\mathrm{B} < \mathrm{C} < \mathrm{A}$

Given the same initial concentration of each acid, the weakest acid would have the highest pH. Therefore, acid B would have the highest pH.

Exercise $8.E.41$***

To find the pH, we need the initial concentration of $\mathrm{CH_3COOH}$ in mol/L to set up an ICE table.

$\left(\frac{5.0\text{ g }\mathrm{CH_3COOH}}{100\text{ g solution}}\right)\left(\frac{\text{mol}}{60.05\text{ g }\mathrm{CH_3COOH}}\right)\left(\frac{1.007\text{ g solution}}{\text{mL}}\right)\left(\frac{1000\text{ mL}}{\text{L}}\right) = 0.84\text{ M}$

	$\mathrm{CH_3COOH\,(aq)} +$	$\mathrm{H_2O\,(l)}$ ⇌	$\mathrm{CH_3COO^-\,(aq)} +$	$\mathrm{H_3O^+\,(aq)}$
Initial	0.84 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.84 - x		x	x

$K_a = \frac{[\mathrm{CH_3COO^-}][\mathrm{H_3O^+}]}{[\mathrm{CH_3COOH}]} = \frac{x^2}{0.84-x} = 1.8\times10^{-5}$

Since K_a is very small, the acid will only ionize slightly and we can assume that $\mathrm{x} << 0.84\text{ M}$.

$K_a = \frac{x^2}{0.84} = 1.8\times10^{-5}\ x = 3.9\times10^{-3}\text{ M}$

Checking assumption:

$\frac{3.9\times10^{-3}}{0.84}\times100\% = 0.46\%$

The assumption is valid since the percentage is less than 5%.

$[\mathrm{H_3O^+}] = \mathrm{x} = 3.9\times10^{-3}\text{ M}$

$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 2.41$

Exercise $8.E.42$**

To compare basicity, we consider the strength of the conjugate acids: $\mathrm{HBrO_2}$, $\mathrm{HClO_2}$, and $\mathrm{IO_2}$.

All three are oxoacids with the same number of oxygen atoms. In such cases, electronegativity of the central atom determines acid strength:

- Chlorine is more electronegative than bromine or iodine.
- Therefore, acid strength increases as:

$$\mathrm{HIO_2} < \mathrm{HBrO_2} < \mathrm{HClO_2}.$$

Since base strength is inversely related to conjugate acid strength, the order of increasing basicity is:

$$\mathrm{ClO_2^-} < \mathrm{BrO_2^-} < \mathrm{IO_2^-}$$

Exercise $8.E.43$***

	$\mathrm{HClO_2\,(aq)} +$	$\mathrm{H_2O\,(l)}$ ⇌	$\mathrm{ClO_2^-\,(aq)} +$	$\mathrm{H_3O^+\,(aq)}$
Initial	0.010 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.010 - x		x	x

$K_a = \frac{[ClO_2^-][H_3O^+]}{[HClO_2]} = \frac{x^2}{0.010-x} = 1.1 \times 10^{-2}$

K_a is relatively large for a weak acid. Let's assume that $x << 0.010$ M and see what happens.

$K_a = \frac{x^2}{0.010} = 1.1 \times 10^{-2}\ x = 1.0 \times 10^{-2}$ M

Checking assumption:

$\frac{1.0\times10^{-2}}{0.010} \times 100\% = 100\%$

The assumption is not valid since the percentage is greater than 5%. We will need to use the quadratic equation:

$K_a = \frac{x^2}{0.010-x} = 1.1 \times 10^{-2}\ x^2 = 1.1 \times 10^{-4} - 1.1 \times 10^{-2}x\ x^2 + 1.1 \times 10^{-2}x - 1.1 \times 10^{-4} = 0$

$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$

Solving the quadratic, we obtain \(\text{x} = 0.0063 M and -0.017 M. The negative root gives a negative concentration, so we can ignore it.

$[HClO_2] = 0.010 - x = 0.0037$ M; $[H_3O^+] = [ClO_2^-] = x = 0.0063$ M

Let's plug these values into the K_a expression to double-check:

$K_a = \frac{[ClO_2^-][H_3O^+]}{[HClO_2]} = \frac{(0.0063M)(0.0063M)}{(0.0037M)} = 1.1 \times 10^{-2}$

This matches the K_a.

$pH = -\log[H_3O^+] = 2.20$

$$\%\ \text{ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% = \frac{0.0063M}{0.010} \times 100\% = 63\%$$

Exercise $8.E.44$**

a. HB and HC are weak acids because they ionize only slightly in water. HC is a stronger acid than HB because it ionizes more. HA ionizes completely so it is a strong acid.

As the K_a of the acid increases, so does its strength:

HB < HC < HA.

b. $NaA \rightarrow Na^+(aq) + A^-(aq)$

Na^+ does not react with water to form either H_3O^+ or OH^-, so it gives a neutral solution. The A^- ion is the conjugate base of a strong acid (HA), so it is such a weak base that its base strength can be considered negligible and does not affect the pH of the solution. The solution is neutral.

c. The weaker conjugate acid will have the stronger base. Therefore B^- is a stronger base than C^-.

Exercise $8.E.45$***

Let's refer to procaine at Pr and its protonated form (from the salt) as HPr^+. The chloride ion (Cl^-) does not affect pH and can be ignored.

	$HPr^+(aq)$ +	$H_2O(l)$ ⇌	Pr (aq) +	$H_3O^+(aq)$
Initial	0.073 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.073 - x		x	x

$K_a(HPr^+) = \frac{K_w}{K_b(Pr)} = \frac{1.0\times10^{-14}}{7.0\times10^{-6}} = 1.4 \times 10^{-9}$

$K_a = \frac{[Pr][H_3O^+]}{[HPr^+]} = \frac{x^2}{0.073-x} = 1.4 \times 10^{-9}$

Since K_a is very small, the acid will only ionize slightly and we can assume that $x << 0.073$ M.

$K_a == \frac{x^2}{0.073} = 1.4 \times 10^{-9}\ x = 1.0 \times 10^{-5}\ M$

Checking assumption:

$\frac{1.0\times10^{-5}}{0.073} \times 100\% = 0.014\%$

The assumption is valid since the percentage is less than 5%.

$[H_3O^+] = x = 1.0 \times 10^{-5}$ M

$pH = -\log[H_3O^+] = 5.00$

Exercise $8.E.46$**

$[H_3O^+] = 10^{-pH} = 10^{-7.42} = 3.8 \times 10^{-8}$ M $3.8 \times 10^{-8} \frac{mol}{L}(5.2\ L) = 2.0 \times 10^{-7}$ mol 2.0×10^{-7} mol $(6.022 \times 10^{23}$ ions/mol$) = 1.2 \times 10^{17}$ ions

Exercise $8.E.47$**

	HA (aq) +	$H_2O(l)$ ⇌	$A^-(aq)$ +	$H_3O^+(aq)$
Initial	0.57 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.57 M - x		x	x

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$\%\ \text{ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% = \frac{[H_3O^+]_{eq}}{0.57\ M} \times 100\% = 2.4\%$$

$$[H_3O^+]_{eq} = 0.01368\ M = x$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{x^2}{0.57-x} = \frac{0.01368^2}{0.57-0.01368} = 3.4 \times 10^{-4}$$

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9: APPLICATIONS OF AQUEOUS EQUILIBRIA

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9.1: Introduction

The Case of the Colorado Brown Stain: How Chemistry Solved a Dental Mystery



Figure 9.1.1**:** A graphic with basic facts about Frederick McKay, the dentist whose discoveries led to the implementation of community water fluoridation (CWF). To this day, CWF is considered to be one of the most successful public health initiatives in human history.

What if an observation by a dentist, not a chemist, led to one of the most influential chemistry-related public health breakthroughs of the 20th century? That's exactly what happened in the early 1900s when dentist Frederick McKay began to investigate an unusual mystery: why did children in certain U.S. towns have brown-stained but remarkably cavity-resistant teeth?

The answer turned out to be fluoride: the towns experiencing this phenomenon were using water sources that possessed naturally high levels of this ion. As researchers looked deeper, they discovered that adding a small, controlled amount of fluoride to drinking water was enough to dramatically reduce tooth decay. This led to the development of community water fluoridation (CWF), a public health measure that still protects millions of people today. Numerous studies over the last century have confirmed its safety and effectiveness. The U.S. Centers for Disease Control considers CWF one of the ten greatest public health achievements of the 20th century.

Canada was among the early adopters of water fluoridation. Brantford, Ontario, became the first Canadian city to fluoridate its water in 1945 as part of a landmark study. The success of this pilot project helped influence other municipalities across the country. Today, fluoridation policies vary by province and municipality and the topic continues to spark public discussion; however, scientific consensus supports CWF as a safe, cost-effective, and equitable method to prevent tooth decay.

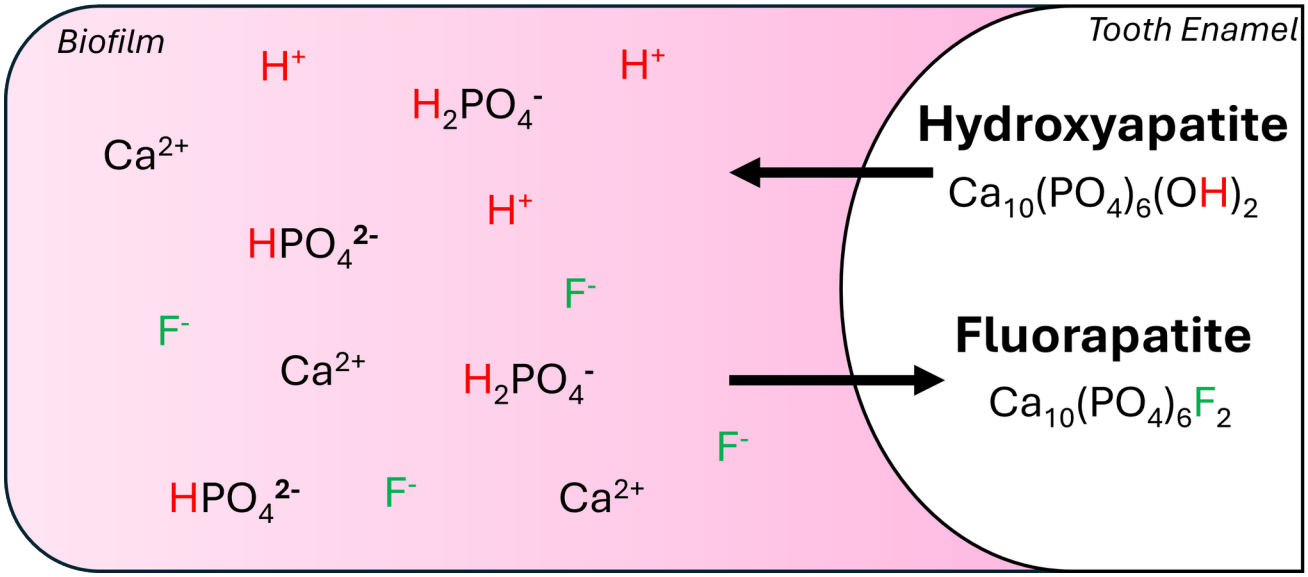


Figure 9.1.2**:** A diagram simplifying the way fluoride strengthens tooth enamel. Tooth enamel is made up of a mineral called hydroxyap which contains phosphate, calcium, and hydroxide. Normally, there is an equilibrium between those ions in the saliva and in the solid t enamel. Under acidic conditions (which happen after eating or drinking), more of the tooth enamel dissolves in a process called demineralization. If the pH is raised back up, usually by saliva, remineralization can occur. You get a cavity when demineralization outw remineralization. If fluoride ions are present, they replace the hydroxide ions in hydroxyapatite to form fluorapatite. This mineral is m resistant to demineralization, making teeth less vulnerable to decay in acidic environments.

Though initiated by dentists, a wealth of chemistry lies behind this success story, especially in the areas of buffers, titration, and solubility, which you will learn about in this chapter. Titration techniques were used to accurately measure fluoride concentrations in water during early research and are still essential today for monitoring safe levels. Solubility principles help explain how fluoride ions dissolve in water and how they interact with hydroxyapatite in teeth, forming stronger and more acid-resistant mineral structures like fluorapatite. Buffer systems are critical in maintaining the stable pH of drinking water. If the pH fluctuates too much, the amount of fluoride that dissolves may become too high (causing the brown stains seen in the original discovery) or too low (becoming an ineffective dose).

In this chapter, we'll explore how buffer systems help stabilize pH and how solubility equilibria govern the behaviour of dissolved ions, which are key concepts in understanding water fluoridation.

Sources:

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9.2: Neutralization Reactions

Learning Objectives

- Identify neutralization reactions.
- Calculate the concentrations present in solution after the reaction of a strong acid and a strong base.
- Predict whether a neutralization reaction will produce an acidic, basic, or neutral solution based on the identity of the salt formed.

A neutralization reaction occurs when an acid and a base react to form a salt and water. Neutralization reactions are important in buffer formation and are a key component in titrations, making them an essential part of this chapter.

Reactions Involving a Strong Acid and a Strong Base

When equal amounts of a strong acid, such as hydrochloric acid (HCl),and a strong base, such as sodium hydroxide (NaOH), are mixed, the result is a solution containing a salt, in this case sodium chloride (NaCl), and water:

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)}$$

This reaction can be represented more explicitly using the net ionic equation. In water, HCl dissociates completely to form $\mathrm{H_3O^+}$ and $\mathrm{Cl^-}$ and NaOH dissociates completely into $\mathrm{Na^+}$ and $\mathrm{OH^-}$. Expanding the reaction to show these ions:

$$\mathrm{H_3O^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \rightarrow Na^+\,(aq) + Cl^-\,(aq) + 2H_2O\,(l)}$$

The $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions are spectator ions and can be removed from the equation. The net ionic equation is the reverse of water autoionization:

$$\mathrm{H_3O^+\,(aq) + OH^-\,(aq) \rightleftharpoons 2H_2O\,(l)} \qquad K_n = \frac{1}{K_w} = 1.0 \times 10^{14}$$

The large K_n value for the neutralization reaction between $\mathrm{H_3O^+}$ and $\mathrm{OH^-}$ is the reason that neutralization reactions tend to be heavily product-favoured. In practice, it is reasonable to treat the reaction as going to completion (using a one-way arrow) and assume that the reaction proceeds until the reactants are consumed.

The pH of a solution created by mixing equal moles of a strong acid and a strong base produces a salt with no acidic or basic properties and so the pH of the resulting salt solution is neutral.

Example 9.2.1: pH of a solution from the reaction of a strong acid and a strong base

Solid KOH is added to 1.0 L of a 1.0 M solution of HBr. Calculate the pH of the solution after the KOH additions below. Assume no change in volume.

a. Addition of 0.50 moles of KOH.

b. Addition of 1.0 moles of KOH.

c. Addition of 1.5 moles of KOH.

Solution

a. This is a neutralization reaction between a strong acid and a strong base so we can assume it goes to completion:

$$\mathrm{HBr\,(aq) + KOH\,(aq) \rightarrow KBr\,(aq) + H_2O\,(l)}$$

The HBr solution contains 1.0 moles of HBr: $n = CV = 1.0\frac{mol}{L} \times 1.0\ L = 1.0\ \ mol$
This 1.0 mol of HBr will react with the 0.5 mol KOH according to the stoichiometry of the reaction:

	$HBr(aq) +$	$KOH(aq)$ ⇌	$KBr(aq) +$	$H_2O(l)$
Initial	1.0 mol	0.50 mol	0 mol	X
Change	- 0.50 mol	- 0.50 mol	+ 0.50 mol	
Final	0.50 mol	0 mol	0.50 mol	

The final solution after reaction includes 0.50 mol HBr and 0.50 mol KBr
KBr has no acid-base properties and so only the 0.50 mol HBr remaining in the 1.0 L of solution will determine the pH:

$$[H_3O^+] = \frac{0.50\ \ mol}{1.0\ \ L} = 0.50\frac{mol}{L}$$

$$pH = -\log[H_3O^+] = -\log(0.50\ M) = 0.30$$

b. Reaction of 1.0 mol KOH with 1.0 mol HBr will result in a solution of KBr which is a salt with no acid-base properties and so the pH of the solution will be 7.00. HBr is a strong acid (very large K_a), and its conjugate base Br^- is an extremely weak base that does not appreciably react with water. K^+ does not react with water to form either H_3O^+ or OH^-, so it also gives a neutral solution.
c. Reaction of 1.5 mol KOH with 1.0 mol HBr will consume all of the HBr and leave an excess of 0.50 mol KOH.

	$HBr(aq) +$	$KOH(aq)$ ⇌	$KBr(aq) +$	$H_2O(l)$
Initial	1.0 mol	1.5 mol	0 mol	X
Change	- 1.0 mol	- 1.0 mol	+ 1.0 mol	
Final	0 mol	0.50 mol	1.0 mol	

With an excess of KOH the reaction will be basic with the pH of the solution dictated by the excess of OH^- beyond neutral:

$$[OH^-] = \frac{0.50\ mol}{1.0\ L} = 0.50\frac{mol}{L}$$

$$pOH = -\log[OH^-] = -\log(0.50\ \ M) = 0.30$$

$$pH = 14.00 - pOH = 14.00 - 0.30 = 13.70$$

Exercise 9.2.1

What is the pH of the following solutions:

a. 0.25 mol HNO_3 mixed with 0.35 mol $NaOH$ in 0.50 L of water.
b. 0.30 mol $HClO_4$ mixed with 0.15 mol $Ca(OH)_2$ in 0.25 L of water.

Answer available at the end of this section.

Reactions Involving a Weak Acid or a Weak Base

To explore the reaction of a weak acid and a strong base, consider the reaction between nitrous acid ($\mathrm{HNO_2}$), and potassium hydroxide (KOH):

$$\mathrm{HNO_2\,(aq) + KOH\,(aq) \rightarrow KNO_2\,(aq) + H_2O\,(l)}$$

Leaving out $\mathrm{K^+}$, the spectator ion:

$$\mathrm{HNO_2\,(aq) + OH^-\,(aq) \rightarrow NO_2{}^-\,(aq) + H_2O\,(l)}$$

To estimate the equilibrium constant (K_n) for this reaction, we combine the weak acid ionization equilibrium with the auto-ionization of water:

$$\mathrm{HNO_2\,(aq) + H_2O \rightleftharpoons NO_2{}^-\,(aq) + H_3O^+\,(aq)} \qquad K_a = 4.5 \times 10^{-4}$$

$$\mathrm{H_3O^+\,(aq) + OH^-\,(aq) \rightleftharpoons 2\,H_2O\,(l)} \qquad \frac{1}{K_w} = 1.0 \times 10^{14}$$

$$\mathrm{HNO_2\,(aq) + OH^-\,(aq) \rightleftharpoons NO_2{}^-\,(aq) + H_2O\,(l)} \qquad K_n = K_a \times \frac{1}{K_w} = 4.5 \times 10^{10}$$

Adding these reactions and multiplying their equilibrium constants shows that K_n for this neutralization reaction is large, meaning the reaction is highly product-favoured.

Like reactions between strong acids and strong bases, this large K_n means the reaction proceeds nearly to completion. It is appropriate to use a single arrow for this reaction:

$$\mathrm{HNO_2\,(aq) + OH^-\,(aq) \rightarrow NO_2{}^-\,(aq) + H_2O\,(l)}$$

Reactions involving a weak base and a strong acid behave similarly. For example:

$$\mathrm{NH_3\,(aq) + HCl\,(aq) \rightarrow NH_4Cl\,(aq)} \qquad K_n = 1.8 \times 10^{9}$$

As long as one of the species in the neutralization reaction is a strong acid or a strong base, the neutralization reaction is product-favoured. If the reaction involves a weak acid and a weak base a more thorough examination of their respective K_a and K_b values would be required.

Note: In this textbook, we discuss neutralization reactions in more detail than in class. For problem solving, you can safely assume that any neutralization reaction involving at least one strong acid or strong base goes essentially to completion.

Unlike neutralization reactions between strong acids and strong bases, when one reactant is a weak acid or a weak base, you must consider the acid-base properties of the salt produced to predict the pH:

A Weak Acid + Strong Base Neutralization

A weak acid and strong base neutralization (e.g., $\mathrm{HNO_2}$ and KOH) produces a salt ($\mathrm{KNO_2}$) containing a weak conjugate base:

$$\mathrm{HNO_2\,(aq) + KOH\,(aq) \rightarrow KNO_2\,(aq) + H_2O\,(l)}$$
$$\mathrm{KNO_2\,(aq) \rightarrow K^+\,(aq) + NO_2{}^-\,(aq)}$$
$$\mathrm{NO_2{}^-\,(aq) + H_2O\,(l) \rightleftharpoons HNO_2\,(aq) + OH^-\,(aq)}$$

The $\mathrm{NO_2{}^-}$ ion is the conjugate base of the weak acid $\mathrm{HNO_2}$. It reacts with water to produce $\mathrm{OH^-}$, which makes the solution basic.

The $\mathrm{K^+}$ does not react with water to form either $\mathrm{H_3O^+}$ or $\mathrm{OH^-}$, so it does not affect the pH.

The pH of the solution is greater than 7 (basic).

A Weak Base + Strong Acid Neutralization

A weak base and strong acid neutralization (e.g., $\mathrm{NH_3}$ and HCl) produces a salt ($\mathrm{NH_4Cl}$) containing a weak conjugate acid:

$$\begin{aligned}\mathrm{NH_3\,(aq) + HCl\,(aq)} &\rightarrow \mathrm{NH_4Cl\,(aq)}\\ \mathrm{NH_4Cl\,(aq)} &\rightarrow \mathrm{NH_4{}^+\,(aq) + Cl^-\,(aq)}\\ \mathrm{NH_4{}^+\,(aq) + H_2O\,(l)} &\rightleftharpoons \mathrm{NH_3\,(aq) + H_3O^+\,(aq)}\end{aligned}$$

The $\mathrm{NH_4{}^+}$ ion is the conjugate acid of the weak base $\mathrm{NH_3}$. It reacts with water to produce $\mathrm{H_3O^+}$, making the solution acidic.

$\mathrm{Cl^-}$ is an extremely weak base (conjugate base of a strong acid) and it does not appreciably react with water. It therefore has no effect on pH.

The pH of the solution is less than 7 (acidic).

Example 9.2.2: pH of a solution from the reaction of a strong acid and a strong base

Predict whether the pH of the following solutions will be acidic, basic or neutral:

a. Reaction of 0.50 mol KOH with 0.50 mol $\mathrm{CH_3COOH}$ in 1.0 L of water.

b. Reaction of 0.50 mol $\mathrm{NH_3}$ with 0.50 mol $\mathrm{HNO_3}$ in 1.0 L of water.

c. Reaction of 0.50 mol $\mathrm{HClO_2}$ with 0.50 mol CsOH in 1.0 L of water.

Solution

a. The neutralization reaction is between equal moles of strong base KOH and weak acid $\mathrm{CH_3COOH}$:

$$\begin{aligned}\mathrm{KOH\,(aq) + CH_3COOH\,(aq)} &\rightarrow \mathrm{H_2O\,(l) + KCH_3COO\,(aq)}\\ \mathrm{KCH_3COO\,(aq)} &\rightarrow \mathrm{K^+\,(aq) + CH_3COO^-\,(aq)}\\ \mathrm{CH_3COO^-\,(aq) + H_2O\,(l)} &\rightleftharpoons \mathrm{CH_3CHOOH\,(aq) + OH^-\,(aq)}\end{aligned}$$

The weak conjugate base $\mathrm{CH_3COO^-}$ reacts with water, producing some $\mathrm{OH^-}$. The solution will be basic.

$\mathrm{K^+}$ does not react with water to form either $\mathrm{H_3O^+}$ or $\mathrm{OH^-}$, so it does not affect the pH.

b. The neutralization reaction is between equal moles of strong acid $\mathrm{HNO_3}$ and weak base $\mathrm{CH_3NH_2}$:

$$\begin{aligned}\mathrm{NH_3\,(aq) + HNO_3\,(aq)} &\rightarrow \mathrm{NH_4NO_3\,(aq)}\\ \mathrm{NH_4NO_3\,(aq)} &\rightarrow \mathrm{NH_4{}^+\,(aq) + NO_3{}^-\,(aq)}\\ \mathrm{NH_4{}^+\,(aq) + H_2O\,(l)} &\rightleftharpoons \mathrm{NH_3\,(aq) + H_3O^+\,(aq)}\end{aligned}$$

The weak conjugate acid $\mathrm{NH_4{}^+}$ reacts with water, producing some $\mathrm{H_3O^+}$. The solution will be acidic.

$\mathrm{NO_3{}^-}$ is an extremely weak base (conjugate base of a strong acid) and it does not appreciably react with water. It therefore has no effect on pH.

c. The neutralization reaction is between equal moles of strong base CsOH and weak acid $\mathrm{HClO_2}$:

$$\begin{aligned}\mathrm{HClO_2\,(aq) + CsOH\,(aq)} &\rightarrow \mathrm{CsClO_2\,(aq) + H_2O\,(l)}\\ \mathrm{CsClO_2\,(aq)} &\rightarrow \mathrm{Cs^+\,(aq) + ClO_2{}^-\,(aq)}\\ \mathrm{ClO_2{}^-\,(aq) + H_2O\,(l)} &\rightleftharpoons \mathrm{HClO_2\,(aq) + OH^-\,(aq)}\end{aligned}$$

The weak conjugate base $\mathrm{ClO_2{}^-}$ reacts with water, producing some $\mathrm{OH^-}$. The solution will be basic.

$\mathrm{Cs^+}$ does not react with water to form either $\mathrm{H_3O^+}$ or $\mathrm{OH^-}$, so it does not affect the pH.

Exercise 9.2.2

Predict whether the pH of a solution containing 0.50 mol $\mathrm{Sr(OH)_2}$ and 1.0 mol HCOOH in 1.0 L of water will be acidic, basic or neutral.

Answer available at the end of this section.

Summary

A neutralization reaction is a reaction between an acid and a base to produce a salt solution.

Neutralization reactions that involve at least one strong acid or strong base are product-favoured and can be assumed to go fully to completion.

The pH of the salt solution produced from a neutralization reaction depends on the nature of the acid and base involved:

- A neutralization reaction of a weak acid (e.g. $\mathrm{HNO_2}$) and a strong base (e.g. KOH) produces a salt containing a weak conjugate base (e.g. $\mathrm{NO_2^-}$). This conjugate base reacts with water to produce $\mathrm{OH^-}$, making the solution basic.
- A neutralization reaction of a weak base (e.g. $\mathrm{NH_3}$) and a strong acid (e.g. HCl) produces a salt containing a weak conjugate acid (e.g. $\mathrm{NH_4^+}$). This conjugate acid reacts with water to produce $\mathrm{H_3O^+}$, making the solution acidic.
- A neutralization reaction of a strong acid and a strong base produces a neutral salt solution, as neither ion from the salt affects the pH.

Glossary

neutralization reaction
: A reaction in which an acid and a base react to form a salt and water.

Answers

Exercise 9.2.1

a. $\mathrm{HNO_3}$ is a strong acid and NaOH is a strong base, so the reaction goes to completion leaving an excess of NaOH:

	$\mathrm{HNO_3(aq)} +$	$\mathrm{NaOH(aq)}$ ⇌	$\mathrm{NaNO_3(aq)} +$	$\mathrm{H_2O(l)}$
Initial	0.25 mol	0.35 mol	0 mol	X
Change	- 0.25 mol	- 0.25 mol	+ 0.25 mol	
Final	0 mol	0.10 mol	0.25 mol	

After the reaction, excess NaOH remains, making the solution basic.

$$[\mathrm{OH^-}] = \frac{0.10\ \mathrm{mol}}{0.50\ \mathrm{L}} = 0.20 \frac{\mathrm{mol}}{\mathrm{L}}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(0.20\ \ \mathrm{M}) = 0.70$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 0.70 = 13.30$$

b. $\mathrm{HClO_4}$ is a strong acid and $\mathrm{Ca(OH)_2}$ is a strong base that provides 2 moles of $\mathrm{OH^-}$ per mole of base:

	$\mathrm{2\,HClO_4(aq)} +$	$\mathrm{Ca(OH)_2(aq)}$ ⇌	$\mathrm{Ca(ClO_4)_2(aq)} +$	$\mathrm{2\,H_2O(l)}$
Initial	0.30 mol	0.15 mol	0 mol	X
Change	- 2x	- x	+ x	
Final	0.30 - 2x	0.15 - x	x	

Since each mol of $\mathrm{Ca(OH)_2}$ reacts with 2 moles of $\mathrm{HClO_4}$, 0.15 mol of $\mathrm{Ca(OH)_2}$ consume 0.30 mol of $\mathrm{HClO_4}$. Both the acid and the base are completely consumed (x = 0.15 mol) and only $\mathrm{Ca(ClO_4)_2}$ and water remain.

$\mathrm{Ca(ClO_4)_2}$ is a neutral salt:

- $\mathrm{ClO_4^-}$ is the conjugate base of a strong acid $\mathrm{HClO_4}$ and is an extremely weak base that does not appreciably react with water.

- Ca^{2+} does not react with water to form either H_3O^+ or OH^-.

As a result, the solution is neutral and the pH = 7.00.

Exercise $9.2.2$

0.50 mol $Sr(OH)_2$ will dissociate into 1.0 mol of OH^-, which will fully neutralize the 1.0 mol of the weak acid $HCOOH$:

$$Sr(OH)_2\,(aq) + 2\,HCOOH \rightarrow 2\,H_2O\,(l) + Sr(HCOO)_2\,(aq)$$

The salt dissociates in solution:

$$Sr(HCOO)_2\,(aq) \rightarrow Sr^{2+}\,(aq) + 2\,HCOO^-\,(aq)$$

Since $HCOO^-$ is the conjugate base of a weak acid, it reacts with water to produce OH^-:

$$HCOO^-\,(aq) + H_2O\,(l) \rightleftharpoons HCOOH\,(aq) + OH^-\,(aq)$$

This reaction increases the hydroxide ion concentration, making the solution basic.

The Sr^{2+} does not react with water to form either H_3O^+ or OH^-, so it does not affect the pH.

The pH of the solution will be greater than 7 (basic).

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9.3: Buffers

Learning Objectives

- Explain the effect of a common ion.
- Calculate the pH of a solution containing a weak acid and its conjugate base.
- Identify solutions that will act as buffers and explain how they resist changes in pH.
- Determine the products of neutralization reactions and the equilibrium position of these reactions.
- Calculate the pH of a buffer before and after the addition of strong acid or strong base
- Calculate the composition of a buffer needed to give a particular pH

A buffer resists change. In acid-base chemistry, a buffer solution resists changes in pH when small to moderate amounts of a strong acid or strong base are added. A buffer solution consists of a mixture of a weak acid or base and its conjugate. For example, a solution of acetic acid and sodium acetate ($\mathrm{CH_3COOH\,(aq)}$ and $\mathrm{CH_3COONa\,(aq)}$) is a buffer made of a weak acid and the salt of its conjugate base and a solution of ammonia and ammonium chloride ($\mathrm{NH_3\,(aq)}$ and $\mathrm{NH_4Cl\,(aq)}$) is a buffer made of a weak base and the salt of its conjugate acid.

Figure $9.3.1$ compares two solutions, one containing a buffer and one without, both initially at pH 8.0. Both solutions contain bromothymol, an indicator that is blue above pH 7.9 and yellow below pH 6. After adding 0.5 mL of 0.1 M HCl solution, the unbuffered solution is yellow (pH ≈ 3.3), indicating a significant pH drop. The buffered solution remains blue (pH ≈ 7.9), demonstrating the buffer's ability to resist pH changes.

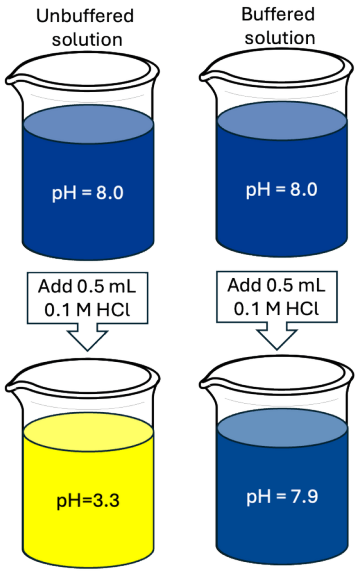


Figure $9.3.1$: An unbuffered solution (left) and a buffered solution (right) start at the same pH (8.0), appearing blue due to bromothymol blue. After adding 0.5 mL of 0.1 M HCl, the unbuffered solution changes to yellow (pH ≈ 3.3), while the buffered solution remains blue (pH ≈ 7.9), showing the buffer's resistance to pH changes.

The Common-Ion Effect

To understand how buffers work, let's first examine how the ionization equilibrium of a weak acid is affected by adding its conjugate base. According to Le Châtelier's principle, adding a common-ion shifts the equilibrium position of a reaction. Consider a buffer used in analytical and biochemistry laboratories, consisting of formic acid and the salt of its conjugate base. The ionization reaction of formic acid is:

$$\mathrm{HCOOH\,(aq) + H_2O\,(l) \rightleftharpoons HCOO^-\,(aq) + H_3O^+\,(aq)} \tag{9.3.1}$$

The equilibrium constant expression is:

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}$$

Sodium formate (HCOONa) is a strong electrolyte that ionizes completely in aqueous solution to produce $\mathrm{Na^+}$ and $\mathrm{HCOO^-}$ ions. Because $\mathrm{Na^+}$ is a spectator ion, it does not affect the equilibrium and can be ignored. Adding sodium formate increases the concentration of $\mathrm{HCOO^-}$. Le Chatelier's principle predicts the equilibrium in Equation 9.3.1 will shift to the left, consuming some of the added $\mathrm{HCOO^-}$ and some of the $\mathrm{H_3O^+}$ ions. At equilibrium, $[\mathrm{H_3O^+}]$ will be lower, meaning the pH will be higher. This makes sense because sodium formate is basic, and adding a base to a weak acid increases the pH.

If a strong acid, such as HCl, is added instead, $[\mathrm{H_3O^+}]$ increases. The equilibrium in Equation 9.3.1 will shift to the left as the additional $\mathrm{H_3O^+}$ reacts with $\mathrm{HCOO^-}$ to form HCOOH.

In both cases, the ionization constant K_a for formic acid remains unchanged; only the equilibrium concentrations are affected. The common-ion effect occurs when an ion is added to an equilibrium system that already contains that ion, causing the equilibrium to shift in the direction that reduces its concentration.

How a Buffer Works

To resist changes in pH, a buffer must contain both an acidic and a basic component to counteract the addition of both strong acid and strong base. However, not all acid-base combinations create a buffer. For example, mixing HCl and NaOH results in neutralization, forming a neutral salt, not a buffer. For a buffer to work, the acid and base must be part of the same equilibrium system. This way, neutralizing one component (by adding strong acid or base) transforms it into the other component, maintaining the buffer mixture.

Thus, a buffer consists of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid.

For example, a solution of formic acid and sodium formate acts as a buffer. If a strong base is added, it reacts with HCOOH, the weak acid in the buffer:

$$\mathrm{HCOOH\,(aq) + OH^-\,(aq) \rightarrow HCOO^-\,(aq) + H_2O\,(l)}$$

Conversely, if a strong acid is added, it reacts with $\mathrm{HCOO^-}$, the weak base in the solution:

$$\mathrm{HCOO^-\,(aq) + H_3O^+\,(aq) \rightarrow HCOOH\,(aq) + H_2O\,(l)}$$

After the strong acid or base reacts, the system re-establishes equilibrium:

$$\mathrm{HCOOH\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCOO^-\,(aq)}$$

This buffering action prevents drastic changes in $\mathrm{H_3O^+}$ concentration. Figure 9.3.2 illustrates how the concentrations of the conjugate acid and base change when a strong acid or base is added. The added strong acid or base reacts with the appropriate component of the buffer system, converting it into the conjugate acid or base. Because the buffer components are weak acids and bases and therefore only ionize slightly, the buffer minimizes pH changes compared to an unbuffered solution.

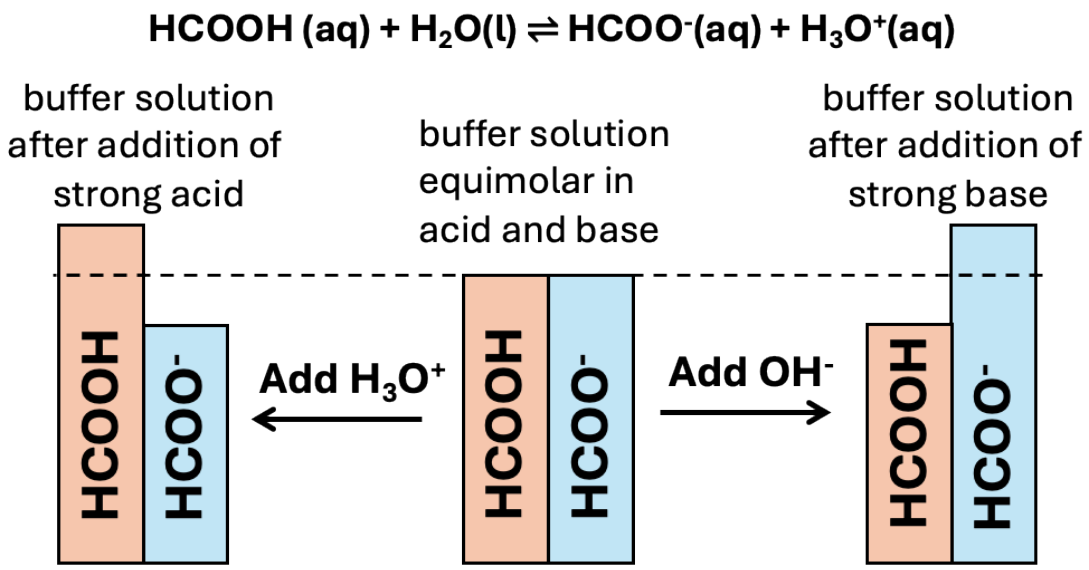


Figure 9.3.2: Buffering action in a mixture of formic acid and sodium formate. The relative concentrations of the weak acid and conjugate base shift when strong acid or base is added, but the pH remains relatively stable.

Example 9.3.1

Formate buffers are used in biochemical and analytical chemistry applications to help maintain a stable pH during chemical reactions and analyses.

Calculate the pH of a formate buffer consisting of 0.25 M formic acid (HCOOH, K_a = 1.8 x 10^{-4}) and 0.15 M sodium formate (HCOONa).

Solution

To find the pH of the buffer solution, we need the $[\mathrm{H_3O^+}]$ at equilibrium. Set up an ICE table, making sure to include the initial $[\mathrm{HCOO^-}]$:

HCOOH (aq) + H_2O(l) ⇌ $HCOO^-$(aq) + H_3O^+(aq)				
Initial	0.25 M	X	0.15 M	0 M
Change	- x		+x	+x
Equilibrium	0.25 - x		0.15 + x	x

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]} = \frac{(x)(0.15+x)}{(0.25-x)} = 1.8 \times 10^{-4}$$

Assume $x << 0.15$, to simplify:

$$\frac{(x)(0.15)}{(0.25)} = 1.8 \times 10^{-4}$$
$$x = 3.0 \times 10^{-4}\ \mathrm{M}$$

Check assumption:

$$\frac{3.0 \times 10^{-4}\ \text{M}}{0.15\ \text{M}} \times 100\% = 0.20\%$$

Since less than 5%, the assumption is valid.

$$\begin{aligned} \text{pH} &= -\log\left[\text{H}_3\text{O}^+\right] \\ &= -\log\left(3.0 \times 10^{-4}\right) \\ &= 3.52 \end{aligned}$$

Example 9.3.2

What is the pH of a formate buffer consisting of 0.25 M formic acid (HCOOH, K_a = 1.8 x 10^{-4}) and 0.15 M sodium formate (HCOONa) after adding 0.020 mol solid NaOH to 1.0 L of the buffer solution. (Assume that the addition of NaOH causes a negligible volume change.)

Solution

To find the pH of the buffer solution, we need the $[\text{H}_3\text{O}^+]$ at equilibrium. Before considering the ionization equilibrium, the strong base, NaOH, must be neutralized by the weak acid:

$$\text{HCOOH}\,(\text{aq}) + \text{OH}^-\,(\text{aq}) \rightarrow \text{HCOO}^-\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l})$$

The single reaction arrow indicates that this reaction goes to completion. We can work in either moles or molarity in this type of reaction table, as long as all species are expressed in the same units. This example uses moles:

$$\text{mol}_{\text{HCOOH}} = (0.25\ \frac{\text{mol}}{\text{L}})(1.0\ \text{L}) = 0.25\ \text{mol}$$

$$\text{mol}_{\text{HCOO}^-} = (0.15\ \frac{\text{mol}}{\text{L}})(1.0\ \text{L}) = 0.15\ \text{mol}$$

	$\text{HCOOH}\,(\text{aq})$ +		$\text{OH}^-\,(\text{aq})$ ⇌	$\text{HCOO}^-\,(\text{aq})$ +
Initial	0.25 mol		0.020 mol	0.15 mol
Change	- 0.020 mol		- 0.020 mol	+ 0.020 mol
Final	0.23 mol		0	0.17 mol

A common mistake is forgetting that the reaction produces HCOO^-.

The moles after the neutralization reaction can be used to find the initial concentrations in the ICE table (note: molarity, not moles, must be used in the ICE table). Since the solution is 1.0 L:

$$[\text{HCOOH}] = \frac{0.23\ \text{mol}}{1.0\ \text{L}} = 0.23\ \text{M}$$
$$[\text{HCOO}^-] = \frac{0.17\ \text{mol}}{1.0\ \text{L}} = 0.17\ \text{M}$$

$\text{HCOOH}\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$ ⇌	$\text{HCOO}^-\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$

Initial	0.23 M	X	0.17 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.23 - x		0.17 + x	x

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]} = \frac{(x)(0.17+x)}{(0.23-x)} = 1.8 \times 10^{-4}$$

Since K_a is small, assume $\mathrm{x} << 0.17$, to simplify:

$$\frac{(x)(0.17)}{(0.23)} = 1.8 \times 10^{-4}$$
$$x = 2.4 \times 10^{-4}\ \mathrm{M}$$

Check assumption:

$$\frac{2.4 \times 10^{-4}\ \mathrm{M}}{0.17\ \mathrm{M}} \times 100\% = 0.14\%$$

Since x is less than 5%, the assumption is valid.

$$\begin{aligned}\mathrm{pH} &= -\log\left[\mathrm{H_3O^+}\right] \\ &= -\log\left(2.4 \times 10^{-4}\right) \\ &= 3.61\end{aligned}$$

The addition of the strong base increased the pH from 3.52 (previous example) to 3.61, so a modest increase.

Comparison with unbuffered solution:

To illustrate the effect of buffering, let's compare this with an unbuffered solution that initially has the same pH (3.52).

The amount of hydronium ion initially present is:

$$\left[\mathrm{H_3O^+}\right] = 10^{-3.52} = 3.0 \times 10^{-4}\ \mathrm{M}$$

Suppose 0.020 mol solid NaOH is added to 1.0 L of this solution. The concentration of hydroxide is:

$$[\mathrm{OH^-}] = \frac{0.020\ \mathrm{mol}}{1.0\ \mathrm{L}} = 0.020\ \mathrm{M}$$

The added hydroxide will neutralize hydronium ion via the reaction:

$$\mathrm{H_3O^+\,(aq) + OH^-\,(aq)\ \rightarrow 2\,H_2O\,(l)}$$

An excess of hydroxide has been added (greater molar amount than the initially present hydronium ion). The amount of hydroxide ion remaining after the neutralization is:

$$0.020\ \mathrm{M} - 3.0 \times 10^{-4}\ \mathrm{M} \approx 0.020\ \mathrm{M}$$

The pH of the solution is then calculated to be

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 12.30$$

Conclusion:
In the unbuffered solution, the pH changes from 3.52 to 12.30.
In the buffered solution, it increases only slightly, from 3.52 to 3.61.

Example 9.3.3

What is the pH of an acetate buffer consisting of 0.10 M acetic acid (CH_3COOH, K_a = 1.8 x 10^{-5}) and 0.10 M sodium acetate (CH_3COONa) after adding 10.0 mL of 0.75 M HCl to 0.80 L of the buffer solution?

Solution

To find the pH of the buffer solution, we need the $[H_3O^+]$ at equilibrium. Before considering the ionization equilibrium, the strong acid must be neutralized by the weak base. Since HCl ionizes completely to produce H_3O^+, so we can write the neutralization reaction in terms of H_3O^+:

$$CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$

The single reaction arrow indicates that this reaction goes to completion. First, calculate the moles of all species:

$$\text{mol}_{CH_3COOH} = \text{mol}_{CH_3COO^-} = (0.10\ \frac{\text{mol}}{\text{L}})(0.80\ \text{L}) = 0.080\ \text{mol}$$
$$\text{mol}_{HCl} = \text{mol}_{H_3O^+} = (0.75\ \frac{\text{mol}}{\text{L}})(0.010\ \text{L}) = 0.0075\ \text{mol}$$

	$CH_3COO^-(aq) +$	$H_3O^+(aq)$ ⇌	$CH_3COOH(aq)$ +	$H_2O(l$
Initial	0.080 mol	0.0075 mol	0.080 mol	X
Change	- 0.0075 mol	- 0.0075 mol	+ 0.0075 mol	
Final	0.0725 mol	0	0.0875 mol	

Now that all the strong acid has reacted, we consider the weak acid/base equilibrium between CH_3COOH and CH_3COO^- to determine the pH of the resulting buffer. The moles after the neutralization reaction can be used to find the initial concentrations in the ICE table (note: molarity, not moles, must be used in the ICE table). The total volume of the solution is 0.80 L (buffer solution) + 0.010 L (HCl) = 0.81 L

$$[CH_3COO^-] = \frac{0.0725\ \text{mol}}{0.81\ \text{L}} = 0.090\ \text{M}$$
$$[CH_3COOH] = \frac{0.0875\ \text{mol}}{0.81\ \text{L}} = 0.108\ \text{M}$$

	$CH_3COOH(aq) +$	$H_2O(l)$ ⇌	$CH_3COO^-(aq) +$	$H_3O^+(aq)$
Initial	0.108 M	X	0.090 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.108 - x		0.090 + x	x

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} = \frac{(x)(0.090 + x)}{(0.108 - x)} = 1.8 \times 10^{-5}$$

Since K_a is small, assume $\mathrm{x} << 0.09$, to simplify:

$$\frac{(x)(0.090)}{(0.108)} = 1.8 \times 10^{-5}$$
$$x = 2.16 \times 10^{-5}\ \mathrm{M}$$

Check assumption:

$$\frac{2.16 \times 10^{-5}\ \mathrm{M}}{0.09\ \mathrm{M}} \times 100\% = 0.024\%$$

Since less than 5%, assumption valid.

$$\begin{aligned}\mathrm{pH} &= -\log\left[\mathrm{H_3O^+}\right] \\ &= -\log\left(2.16 \times 10^{-5}\right) \\ &= 4.67\end{aligned}$$

The addition of the strong acid decreased the pH from 4.74 (previous example) to 4.67, a small decrease.

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 9.3.3). The ability of a buffer solution to resist changes in pH relies on having appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either component of the buffer, the buffering action is compromised.



Figure 9.3.3: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little effect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution, and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one pH unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base present in a buffer mixture. For example, 1 L of a solution that is 1.0 M in acetic acid and 1.0 M in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate, even though both solutions have the same pH. The first solution has a greater buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two key guidelines for selecting a good buffer:

1. **A buffer should contain similar concentrations of both components.**

The buffer becomes ineffective when one component drops below about 10% of the other. Figure 9.3.4 illustrates the limits of buffer capacity by showing how the pH of an acetic acid-acetate buffer changes as NaOH is added. Initially, the pH is 4.74. When the acetic acid concentration decreases to 11% of the acetate concentration, the pH rises by about 1 unit, indicating that the buffer is no longer effective.

A graph is shown with a horizontal axis labeled “Added m L of 0.10 M N a O H” which has markings and vertical gridlines every 10 units from 0 to 110. The vertical axis is labeled “p H” and is marked every 1 unit beginning at 0 extending to 11. A break is shown in the vertical axis between 0 and 4. A red curve is drawn on the graph which increases gradually from the point (0, 4.8) up to about (100, 7) after which the graph has a vertical section up to about (100, 11). The curve is labeled [C H subscript 3 C O subscript 2 H] is 11 percent of [C H subscript 3 <span class=
CO subscript 2 superscript negative]." data-media-type="image/jpeg" style="width: 668px; height: 478px;" width="668px" height="478px" data-cke-saved-src="/@api/deki/files/451056/2c8be66c05f55fd6cebb39371fb0f8de92be2483" src="/@api/deki/files/451056/2c8be66c05f55fd6cebb39371fb0f8de92be2483" data-quail-id="563" class="cke_a11yc_issue cke_a11yc_error">

Figure 9.3.4: Change in pH as an increasing amount of a 0.10 M NaOH solution is added to 100 mL of a buffer solution in which, initially, [$\mathrm{CH_3COOH}$] = 0.10 M and Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. Choose a buffer with a *pKa* close to the desired pH.

You may have noticed in the exercises from the section above that when there are similar concentrations of a weak acid and its conjugate base their concentrations cancel from the K_a expression and $K_a = [\mathrm{H_3O^+}]$. Take the general weak acid HA as an example:

$$\mathrm{HA + H_2O \rightleftharpoons A^- + H_3O^+}$$

When $[\mathrm{HA}] = [\mathrm{A^-}]$:

$$K_a = \frac{[\mathrm{A^-}][\mathrm{H_3O^+}]}{[\mathrm{HA}]} = [\mathrm{H_3O^+}]$$

Since buffers are strongest when the concentrations of the weak acid-base conjugate pairs are similar, the best buffers are formed at pH values similar to the pK_a of the acid.

As a reminder, the K_a and K_b of the acid-base conjugate pair are related through the relationship $K_a \times K_b = K_w$. To make a buffer from the weak base, such as $\mathrm{NH_3}$ ($K_b = 1.8 \times 10^{-5}$), the optimal pH value would be the K_a of its conjugate acid ammonium, $\mathrm{NH_4^+}$:

$$K_a(\mathrm{NH_4^+}) = \frac{K_w}{K_b(\mathrm{NH_3})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{9.3.2}$$

The Henderson-Hasselbalch Equation

To understand buffer behaviour, we must consider how the presence of a common ion affects equilibrium. In buffer solutions, the weak acid (HA) and its conjugate base ($\mathrm{A^-}$) are both present at relatively high concentrations. The common-ion effect suppresses the ionization of the weak acid, meaning that its equilibrium concentration remains close to its initial concentration. This allows us to make a useful approximation when calculating pH.

The ionization constant expression for a weak acid is:

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]}$$

Rearranging to solve for $[\mathrm{H_3O^+}]$:

$$[\mathrm{H_3O^+}] = K_a \times \frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$$

Taking the negative logarithm of both sides:

$$-\log\left[\mathrm{H_3O^+}\right] = -\log K_a - \log\frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$$

which simplifies to:

$$\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

where pK_a is the negative of the logarithm of the ionization constant of the weak acid $pK_a = -\log K_a$ and the fraction in $-\log\frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$ is reversed to $+\log\frac{[A^-]}{[HA]}$ because of the change in sign in front of the logarithm.

This equation, known as the Henderson–Hasselbalch equation, provides a simple way to calculate the pH of a buffer solution. When the "x is small" assumption holds (i.e., when the change in concentrations due to ionization is negligible), we can use initial acid and base concentrations without solving an ICE table.

Example 9.3.4

What is the pH of an acetate buffer consisting of 0.20 M acetic acid (($\mathrm{CH_3COOH}$, K_a = 1.8 x 10^{-5}) and 0.10 M sodium acetate (($\mathrm{CH_3COONa}$).

Solution

$$\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = -\log(1.8\times10^{-5}) + \log\frac{0.10\ \mathrm{M}}{0.20\ \mathrm{M}} = 4.44$$

Example 9.3.5

1.00 mL of 0.75 M $\mathrm{HNO_3}$ is added to the 100.0 mL of the acetate buffer from consisting of 0.20 M acetic acid (($\mathrm{CH_3COOH}$, K_a = 1.8 x 10^{-5}) and 0.10 M sodium acetate ($\mathrm{CH_3COONa}$). What is the pH after the addition?

Solution

When strong acid is added to a buffer, the weak base component neutralizes the acid. Since $\mathrm{HNO_3}$ is a strong acid, it completely forms $\mathrm{H_3O^+}$, so we can write the neutralization reaction as:

$$\mathrm{CH_3COO^-\,(aq) + H_3O^+\,(aq)\ \rightarrow CH_3COOH\,(aq) + H_2O\,(l)}$$

This reaction goes to completion due to the presence of the strong acid. Find the moles of all species:

$$\mathrm{mol_{CH_3COOH}} = (0.20\ \frac{\mathrm{mol}}{\mathrm{L}})(0.100\ \mathrm{L}) = 0.020\ \mathrm{mol}$$
$$\mathrm{mol_{CH_3COO^-}} = (0.10\ \frac{\mathrm{mol}}{\mathrm{L}})(0.100\ \mathrm{L}) = 0.010\ \mathrm{mol}$$
$$\mathrm{mol_{HNO_3}} = \mathrm{mol_{H_3O^+}} = (0.75\ \frac{\mathrm{mol}}{\mathrm{L}})(0.0010\ \mathrm{L}) = 0.00075\ \mathrm{mol}$$

	$\mathrm{CH_3COO^-\,(aq)}$ +	$\mathrm{H_3O^+\,(aq)}$ ⇌	$\mathrm{CH_3COOH\,(aq)}$ +	$\mathrm{H_2O\,(l}$
Initial	0.010 mol	0.00075 mol	0.020 mol	X
Change	- 0.00075 mol	- 0.00075 mol	+ 0.00075 mol	

Final	0.00925 mol	0	0.02075mol	

The total volume of the solution is 101.0 mL, so the molarities are:

$$[CH_3COO^-] = \frac{0.00925\ \text{mol}}{0.101\ \text{L}} = 0.0916\ \text{M}$$
$$[CH_3COOH] = \frac{0.02075\ \text{mol}}{0.101\ \text{L}} = 0.205\ \text{M}$$

These concentrations are used in the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = -\log(1.8 \times 10^{-5}) + \log\frac{0.0916\ \text{M}}{0.205\ \text{M}} = 4.39$$

Note: Since the Henderson–Hasselbalch equation depends on the ratio $\frac{[A^-]}{[HA]}$ and both species are in the same solution, the volumes cancel out. That means you can use moles instead of concentrations when calculating pH, as long as both are present in the same total volume.

The pH of the buffer before adding acid was 4.44 (from the ratio of 0.010 mol CH_3COO^- to 0.020 mol CH_3COOH). The addition of acid changes the pH of the buffer by (4.44-4.39) = -0.05 pH units.

Portrait of a Chemist: Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist, and physiologist. After earning his medical degree from Harvard, he studied in Strasbourg before returning to Harvard as a lecturer and later professor. Henderson discovered that the acid–base balance in blood is regulated by a buffer system involving dissolved carbon dioxide and formulated an equation to describe the carbonic acid–bicarbonate equilibrium in 1908. His interests extended beyond physiology—he also wrote on evolutionary adaptation, sociology, and education, and he founded Harvard's Fatigue Laboratory, which studied work, exercise, and nutrition.

Karl Albert Hasselbalch (1874–1962) was a Danish physician and chemist. He co-authored a 1904 paper with Christian Bohr describing what became known as the Bohr effect, showing how hemoglobin's oxygen-binding capacity varies with acidity and carbon dioxide concentration. Following the introduction of the pH scale in 1909, Hasselbalch published pH measurements of blood and, in 1916, rewrote Henderson's buffer equation in logarithmic form, giving rise to the Henderson–Hasselbalch equation still used today.

Chemistry in Everyday Life: The Buffer System in Blood

The normal pH of human blood is tightly regulated around 7.4. Even small deviations, more than about 0.4 pH units, can be life-threatening. One of the key systems that maintains this balance is the carbonate buffer system, which relies on the following equilibria. Carbon dioxide, a product of cellular respiration, reacts with water to form carbonic acid:

$$CO_2\,(g) + 2\,H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

Carbonic acid (H_2CO_3) is a weak acid that partially ionizes in water to form bicarbonate (HCO_3^-). When significant amounts of both carbonic acid and bicarbonate are present, the solution acts as a buffer:

$$H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)$$

At physiological conditions, typical concentrations are approximately:

- H_2CO_3 ≈ 0.0012 M
- HCO_3^- ≈ 0.024 M

Although the concentration of H_2CO_3 is significantly lower than that of the HCO_3^-, most metabolic by-products that enter the bloodstream are acidic. A higher proportion of base helps prevent the buffer from being overwhelmed.

Here's how the buffer works:

- When an acid is added, bicarbonate neutralizes it:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2\ CO_3(aq) + H_2O(l)$$

- When a base is added, carbonic acid neutralizes it:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The added strong acid or base is converted to the weaker acid or base of the buffer pair, minimizing changes in pH changes.

For example, lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the bicarobnate ion HCO_3^-, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be removed by breathing.

In fact, breathing rate also helps regulate blood pH:

- If blood becomes too acidic, breathing rate increases, expelling more CO_2 and shifting the equilibrium to reduce [H_3O^+].
- If blood is too basic, slower breathing retains CO_2 increasing [H_3O^+] and lowering pH.

Together, the buffer system and respiratory control form a dynamic and highly effective system to resist pH change in the body.

Summary

The common ion effect occurs when a component of an equilibrium system is added, causing the equilibrium to shift away from producing more of that component. For a weak acid, the common ion is its conjugate base. The presence of this conjugate base suppresses the ionization of the weak acid, making it ionize less than it would in pure water.

A buffer solution resists pH changes by neutralizing added acids and bases. It contains:

- A weak acid and its conjugate base → The weak acid neutralizes added OH^- by forming more conjugate base, while the conjugate base neutralizes added H_3O^+ by forming more weak acid.
- A weak base and its conjugate acid → The weak base neutralizes added H_3O^+ by forming more conjugate acid, while the conjugate acid neutralizes added OH^- by forming more weak base.

This prevents large changes in [H_3O^+] and therefore stabilizes the pH.

Buffer effectiveness depends on two factors:

- pK_a close to the desired pH → ensures nearly equal amounts of the weak acid and base.
- Higher concentration = higher buffer capacity → allows the buffer to resist larger amounts of added acid or base.

The Henderson–Hasselbalch equation simplifies buffer pH calculations when ionization is small compared to the initial concentrations. This avoids the need for an ICE table in many cases.

Glossary

buffer
: A mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small

amounts of acid or base are added.

buffer capacity
: The amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit).

common ion effect
: The effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base.

Henderson-Hasselbalch equation
: An equation used to calculate the pH of buffer solutions.

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9.4: Acid-Base Titrations

Learning Objectives

- Contrast the shapes of titration curves for strong and weak acids and bases and the equivalence point pH values.
- Calculate the pH at various points in titrations with strong acids and bases and weak acids and bases.
- Explain how acid-base indicators work and how they are used in titrations.

Titrations allow us to quantify acid-base and redox reactions by carefully measuring the amount of one reactant needed to react completely with another. In this section, we will focus on acid-base titrations, which involve the controlled addition of an acid or base to a solution while monitoring pH changes.

An acid-base titration curve is a graph of pH versus volume of titrant added. In a titration, a buret is used to deliver precise volumes of an acid or base of known concentration (the titrant) into a solution containing a base or acid of unknown concentration (the unknown). By monitoring how the pH changes, we can determine the concentration of the unknown. The shape of the titration curve provides valuable insights into what is happening in solution during the titration.

Titrations of Strong Acids and Bases

To understand how pH changes during a titration, consider first how pH changes when a strong acid or base is gradually added to water:

- Adding 0.20 M HCl dropwise to 50.00 mL of pure water lowers the pH rapidly. Initially, the pH is 7.00 (pure water), but as HCl is added, the pH quickly drops before stabilizing at 0.70 (the pH of 0.20 M HCl). (Figure $9.4.1a$)
- Adding 0.20 M NaOH to 50.00 mL of pure water raises the pH. Initially, the pH is 7.00, but as NaOH is added, the pH rapidly increases before leveling off at 13.30 (the pH of 0.20 M NaOH). (Figure $9.4.1b$)

As seen in Figure $9.4.1$, the graph of pH when adding a strong acid is the mirror image of the graph for adding a strong base.

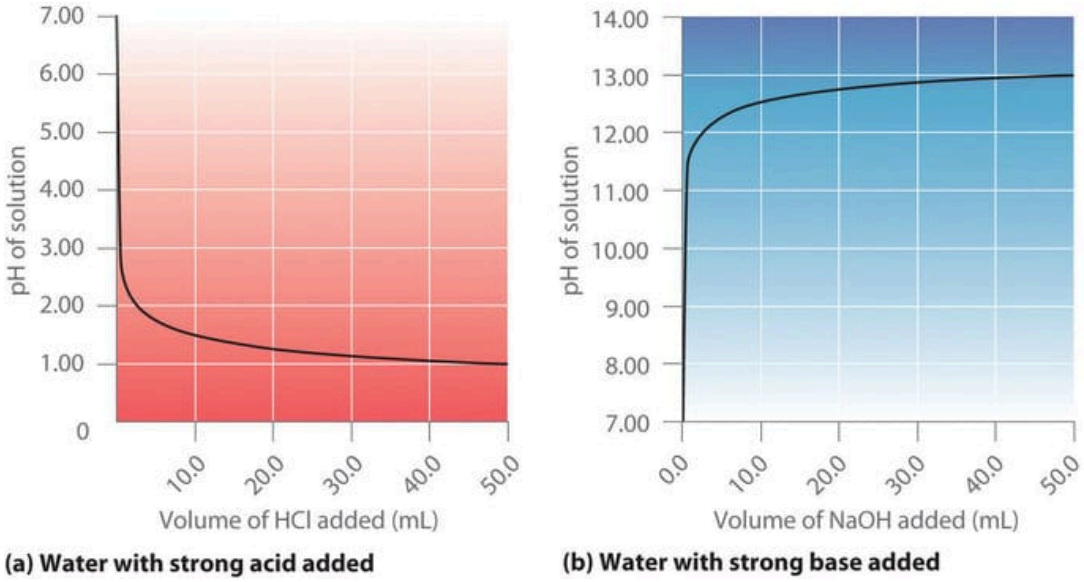


Figure $9.4.1$: pH vs. volume of a strong acid or a strong base added to distilled water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M NaOH. (CC BY-SA-NC; Anonymous by request)

Now, let's examine what happens when 0.20 M NaOH is added to 50.0 mL of 0.10 M HCl. Because HCl is a strong acid, it fully ionizes in water, meaning that the initial $[\mathrm{H_3O^+}]$ is 0.10 M, and the initial pH is 1.00. NaOH is also fully dissociated in water and

so as the NaOH solution is added, the following neutralization reaction occurs:

$$\mathrm{OH^-\,(aq) + H_3O^+\,(aq) \;\rightleftharpoons\; 2\,H_2O\,(l)}$$

The neutralization reaction decreases the $[\mathrm{H_3O^+}]$ and gradually increases the pH. The titration curve for this reaction, shown in Figure $9.4.2a$, has the following key features:

- Initially, the pH is low due to the high concentration of $\mathrm{H_3O^+}$ from the strong acid.
- As NaOH is added, the pH rises gradually as the acid is neutralized.
- Near the equivalence point, the pH increases sharply:
  - The equivalence point occurs when the moles of $\mathrm{OH^-}$ added equal the moles of $\mathrm{H_3O^+}$ originally present from the acid.
  - This rapid pH change happens because the solution shifts from excess $\mathrm{H_3O^+}$ (pH < 7) to excess $\mathrm{OH^-}$ (pH > 7) in just a few drops of titrant.
- At the equivalence point, pH = 7.00:
  - The strong acid (HCl) and the strong base (NaOH) have completely reacted, leaving only $\mathrm{NaCl\,(aq)}$ and water.
  - Recall from Section 9.1 that neutralization reactions of strong acids and bases produce neutral salt solutions.
  - Since the moles of $\mathrm{OH^-}$ added equal the moles of $\mathrm{H_3O^+}$ originally present, we can use this point to determine the initial concentration of the acid.
    - The known volume and concentration of NaOH added at the equivalence point allow us to calculate the original molarity of HCl using reaction stoichiometry.
- After the equivalence point, the pH increases more gradually as excess NaOH is added. Eventually, the pH levels off as the solution approaches the pH of the NaOH solution.

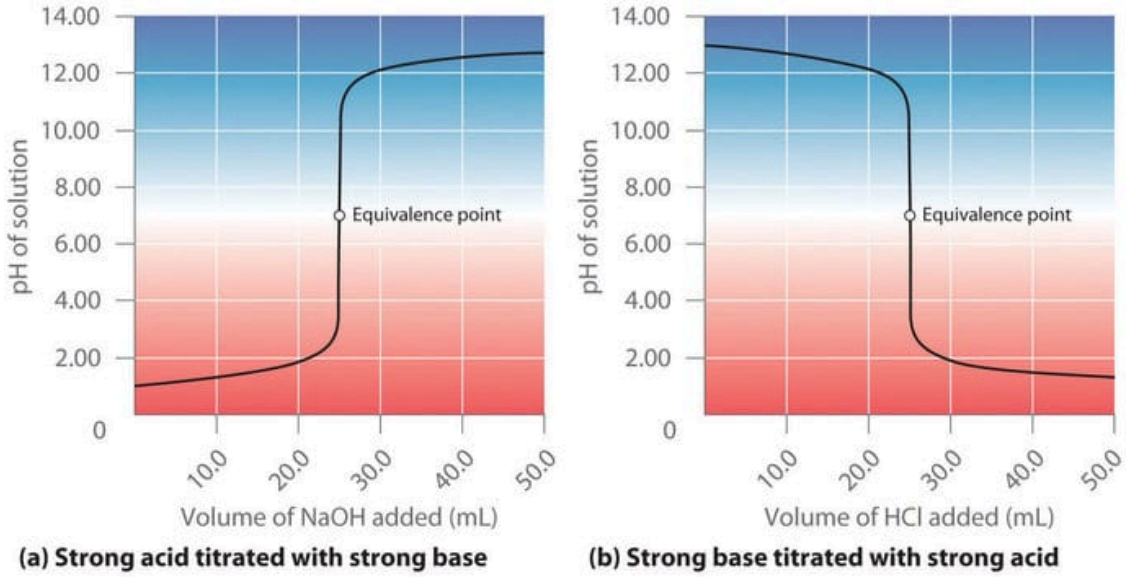


Figure $9.4.2$: The titration of (a) a strong acid with a strong base and (b) a strong base with a strong acid. As 0.20 M NaOH is added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is added to 50.0 mL of 0.10 M NaOH, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

As shown in Figure $9.4.2b$, titrating 50.0 mL of 0.10 M NaOH with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in Figure $9.4.2a$:

- Initially, the pH is 13.00, since NaOH is a strong base.
- As HCl is added, the pH gradually decreases as neutralization occurs.
- Near the equivalence point, the pH drops sharply before leveling off at 0.70, the pH of 0.20 M HCl.

The titration of a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is slightly asymmetrical because the solution is diluted as more titrant is added. Since strong acids and bases ionize completely, the shape of the curve depends only on their concentrations, not their identities.

Example 9.4.1: Hydrochloric Acid

What is the pH of the solution after 24.90 mL of 0.200 M NaOH has been added to 50.00 mL of 0.100 M HCl?

Given: volumes and concentrations of strong base and acid

Asked for: pH

Solution

The neutralization reaction goes to completion. Find the moles of each reactant and determine which is in excess:

$$\mathrm{mol_{NaOH}} = \mathrm{mol_{OH^-}} = (0.200\ \frac{\mathrm{mol}}{\mathrm{L}})(0.02490\ \mathrm{L}) = 0.00498\ \mathrm{mol}$$
$$\mathrm{mol_{HCl}} = \mathrm{mol_{H_3O^+}} = (0.100\ \frac{\mathrm{mol}}{\mathrm{L}})(0.05000\ \mathrm{L}) = 0.00500\ \mathrm{mol}$$

	$\mathrm{OH^-(aq)} +$	$\mathrm{H_3O^+(aq)}$ ⇌	$2\,\mathrm{H_2O(l)}$
Initial	0.00498 mol	0.00500 mol	X
Change	- 0.00498 mol	- 0.00498 mol	
Final	0	0.00002 mol	

After neutralization, an excess $\mathrm{H_3O^+}$ remains. The total volume (0.02490 L + 0.05000 L = 0.07490L) of the solution, so its concentration is:

$$[\mathrm{H_3O^+}] = \frac{0.00002\ \mathrm{mol}}{0.07490\ \mathrm{L}} = 2.7 \times 10^{-4}\ \mathrm{M}$$

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 3.57$$

This is significantly less than the pH of 7.00 for a neutral solution because an excess of strong acid remains after the neutralization reaction.

Exercise 9.4.1

Calculate the pH of a solution prepared by adding 40.00 mL of 0.237 M HCl to 75.00 mL of 0.133 M NaOH.

Answer available at the end of this section.

Titrations of Weak Acids and Bases

Unlike strong acids and bases, the shape of a titration curve for a weak acid or weak base depends on its K_a or K_b. The pH change near the equivalence point is also much more gradual compared to strong acid-strong base titrations.

As discussed earlier, a weak acid (HA) only partially ionizes, meaning the $\mathrm{H_3O^+}$ concentration is lower than the acid concentration. $[\mathrm{H_3O^+}]$ depends on both K_a and concentration. Since weak acids ionize less than strong acids, a solution of a weak acid has a higher initial pH than a strong acid of the same concentration.

A general weak acid-strong base titration curve is shown in Figure 9.4.3. As the titration proceeds, the following neutralization reaction occurs:

$$\mathrm{HA\,(aq) + OH^-\,(aq)\ \rightarrow H_2O\,(l) + A^-\,(aq)}$$

Key features of the titration curve:

- Before titration begins, the weak acid solution has a higher initial pH than a strong acid solution because HA only partially ionizes.
- Before the equivalence point, the pH increases gradually as HA is neutralized and its conjugate base ($\mathrm{A^-}$) forms. This creates a $\mathrm{HA/A^-}$ buffer, which resists rapid pH changes.
- At the titration midpoint,
  - Half of the weak acid (HA) has been neutralized forming $\mathrm{A^-}$, meaning $[\mathrm{HA}] = [\mathrm{A^-}]$.
  - $\mathrm{pH} = pK_a + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right) = pK_a + \log 1 = pK_a$
  - $\mathrm{pH} = pK_a$
- At the equivalence point, the pH is greater than 7.00. HA and $\mathrm{OH^-}$ have reacted completely, leaving only $\mathrm{A^-}$ and water.
  - Recall from Section 9.1 that neutralization reactions involving weak acids and strong bases produce basic salt solutions.
  - The conjugate base ($\mathrm{A^-}$) reacts with water, forming a slightly basic solution: $\mathrm{A^-\,(aq) + H_2O\,(l)\ \rightleftharpoons\ HA\,(aq) + OH^-\,(aq)}$
- After the equivalence point, the pH increases slowly as excess $\mathrm{OH^-}$ dominates the solution.

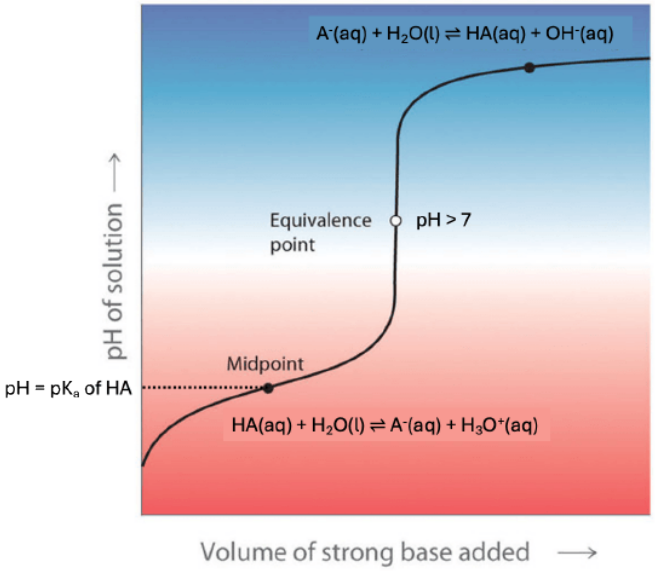


Figure 9.4.3: Titration curve for a weak acid (HA) with NaOH. The nearly flat region of the titration curve around the midpoint (where pH = pK_a) corresponds to the formation of a buffer.

Figure 9.4.4*a* compares the titration curve for 50.0 mL of 0.100 M acetic acid titrated with 0.200 M NaOH to the curve for for 50.0 of 0.100 M HCl from Figure 9.4.2*a*

- Before the equivalence point, the titration curves look very different because acetic acid (a weak acid) only partially ionizes, while HCl (a strong acid) ionizes completely.
- After the equivalence point, the curves become identical because the pH is determined by the excess NaOH in solution.

Figure 9.4.4*b* compares the titration curves for a strong base-strong acid titration and a weak base-strong acid titration.

- Similar to the weak acid case, the titration curve for the weak base differs significantly from the strong base before the equivalence point because the weak base only partially ionizes, while the strong base fully dissociates in solution.
- After the equivalence point, the curves become identical because the pH is determined by the excess strong acid in solution.

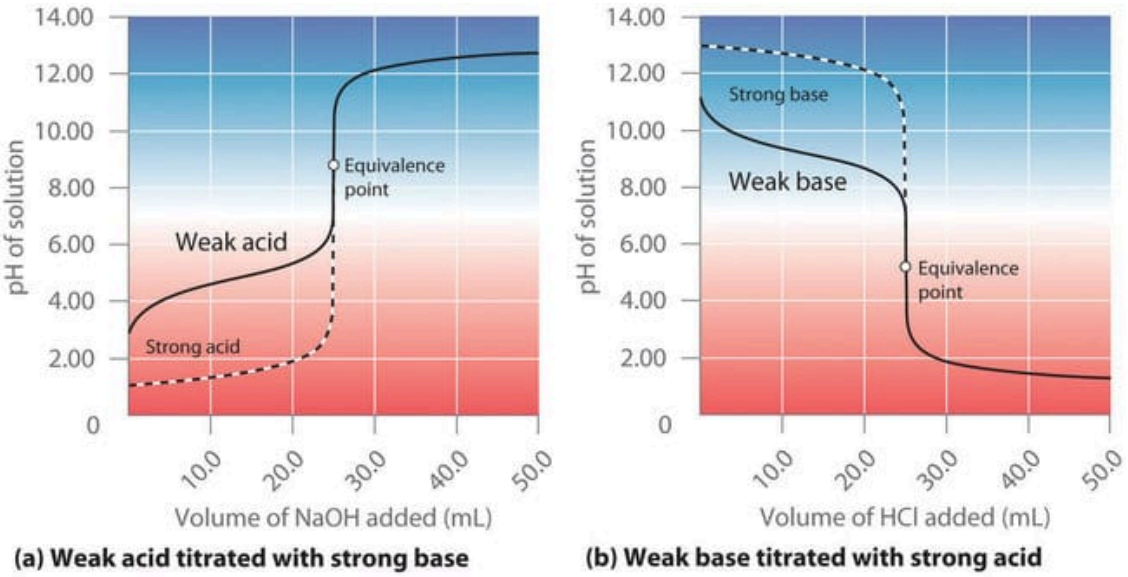


Figure 9.4.4: The titration of (a) a weak acid with a strong base and (b) a weak base with a strong acid. (a) As 0.200 M NaOH is added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is added to 50.0 mL of 0.100 M $\mathrm{NH_3}$, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure 9.4.5 shows how the curves change as a function of the pK_a or pK_b of the species being titrated. As the acid (Figure 9.4.5a) or the base (Figure 9.4.5b) being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point becomes much less pronounced. In very dilute solutions, the curve can become so gradual that it is difficult to accurately pinpoint the equivalence point.

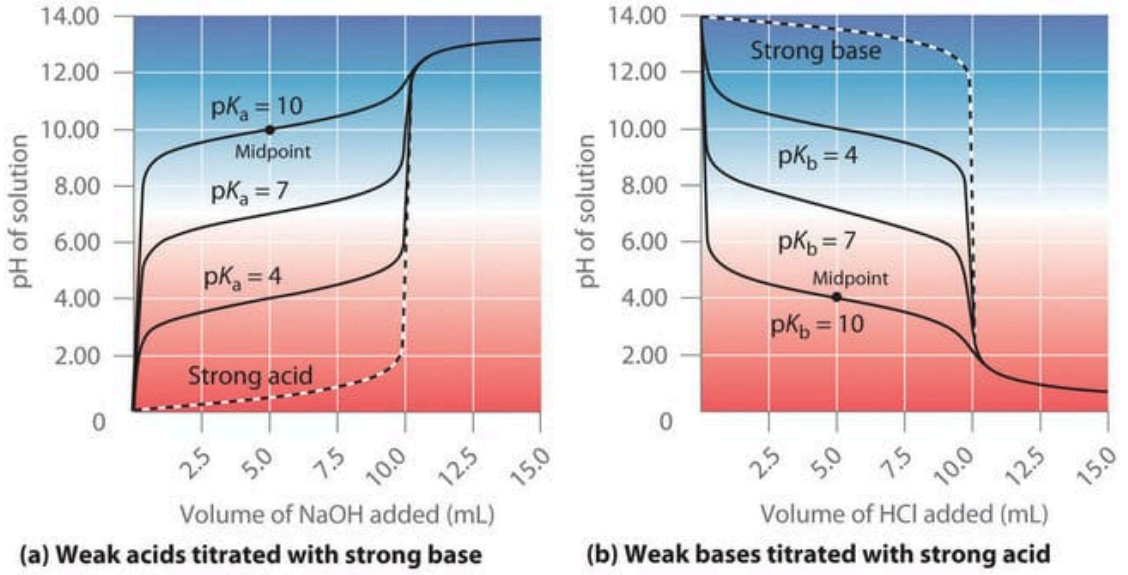


Figure 9.4.5: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10. (CC BY-SA-NC; Anonymous by request)

Calculating pH During Weak Acid-Strong Base Titrations

Titration calculations for a weak acid-strong base reaction require an understanding of equilibrium calculations and neutralization reactions. Let's analyze five key points along the titration curve for 50.00 mL of 0.100 M acetic acid (K_a = 1.8 x 10^{-5}) titrated with 0.200 M NaOH.

1. Initial pH (before base is added)

Before NaOH is added, we only consider the ionization of the weak acid ($\mathrm{CH_3COOH}$):

$\mathrm{CH_3COOH\,(aq)} +$		$\mathrm{H_2O\,(l)}$ ⇌	$\mathrm{CH_3COO^-\,(aq)} +$	$\mathrm{H_3O^+\,(aq)}$
Initial	0.100 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.100 M - x		x	x

Applying the equilibrium expression:

$$K_a = \frac{[\mathrm{CH_3COO^-}][\mathrm{H_3O^+}]}{[\mathrm{CH_3COOH}]} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

Since K_a is small, the acid will only ionize slightly and we can assume that $\mathrm{x} << 0.100\ \mathrm{M}$.

$$K_a = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$
$$x = 1.34 \times 10^{-3}\ \mathrm{M}$$

Checking assumption:

$$\frac{1.34 \times 10^{-3}}{0.100} \times 100\% = 1.34\%\ (\text{valid, since less than 5}$$

$$[\mathrm{H_3O^+}] = 1.34 \times 10^{-3}\ \mathrm{M}$$

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 2.87$$

2. pH before equivalence point (after adding 8.00 mL of NaOH)

As discussed in section 9.1 the neutralization reaction between a weak acid and a strong base has a large K and so the results of this reaction need to be resolved before the K_a equilibrium is considered and pH is calculated using the relative concentrations of the weak acid and conjugate base in solution.

Step 1: Find the moles of the acid and base:

$$\mathrm{mol_{CH_3COOH}} = (0.100\ \frac{\mathrm{mol}}{\mathrm{L}})(0.05000\ \mathrm{L}) = 0.00500\ \mathrm{mol}$$

$$\mathrm{mol_{NaOH}} = \mathrm{mol_{OH^-}} = (0.200\ \frac{\mathrm{mol}}{\mathrm{L}})(0.00800\ \mathrm{L}) = 0.00160\ \mathrm{mol}$$

Step 2: Determine the moles of species after the neutralization reaction. Note that this reaction goes to completion due to the presence of a strong base:

	$CH_3COOH\,(aq)$ +	$OH^-\,(aq)$ ⇌	$CH_3COO^-\,(aq)$ +	$H_2O\,(l)$
Initial	0.00500 mol	0.00160 mol	0 mol	X
Change	- 0.00160 mol	- 0.00160 mol	+ 0.00160 mol	
Final	0.00340 mol	0	0.00160 mol	

Step 3: Determine equilibrium concentrations to find pH. First, calculate concentrations using the total volume (0.0500 L + 0.0080 L = 0.0580 L):

$$[CH_3COOH] = \frac{0.00340\ \text{mol}}{0.0580\ \text{L}} = 0.0586\ \text{M}$$
$$[CH_3COO^-] = \frac{0.00160\ \text{mol}}{0.0580\ \text{L}} = 0.0276\ \text{M}$$

	$CH_3COOH\,(aq)$ +	$H_2O\,(l)$ ⇌	$CH_3COO^-\,(aq)$ +	$H_3O^+\,(aq)$
Initial	0.0586 M	X	0.0276 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0586 M - x		0.0276 M + x	x

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{(x)(0.0276 + x)}{0.0586 - x} = 1.8 \times 10^{-5}$$

Since K_a is very small, the acid will only ionize slightly and we can assume that $x << 0.0276\ \text{M}$.

$$K_a = \frac{(x)(0.0276)}{0.0586} = 1.8 \times 10^{-5}$$
$$x = 3.82 \times 10^{-5}\ \text{M}$$

Checking assumption:

$$\frac{3.82 \times 10^{-5}}{0.0276} \times 100\% = 0.138\%\ (\text{valid})$$

$$[H_3O^+] = 3.82 \times 10^{-5}\ \text{M}$$

$$\text{pH} = -\log[H_3O^+] = 4.42$$

Alternatively, the Henderson-Hasselbalch equation can be used with the initial concentrations of CH_3COOH and CH_3COO^- after neutralization because the degree of ionization is small:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = -\log(1.8 \times 10^{-5}) + \log\frac{0.0276\ \text{M}}{0.0586\ \text{M}} = 4.42$$

3. Halfway to equivalence point (adding 12.50 mL NaOH)

Same process as the example above, but in this case we will see that half-way to the equivalence point we will have equal moles of weak acid and its conjugate base:

Step 1: Find the moles of the acid and base:

$$\text{mol}_{CH_3COOH} = (0.100\ \frac{\text{mol}}{\text{L}})(0.05000\ \text{L}) = 0.00500\ \text{mol}$$

$$\text{mol}_{NaOH} = \text{mol}_{OH^-} = (0.200\ \frac{\text{mol}}{\text{L}})(0.01250\ \text{L}) = 0.00250\ \text{mol}$$

Step 2: Determine the moles of species after the neutralization reaction.

	$CH_3COOH(aq)$ +	$OH^-(aq)$ ⇌	$CH_3COO^-(aq)$ +	$H_2O(l)$
Initial	0.00500 mol	0.00250 mol	0 mol	X
Change	- 0.00250 mol	- 0.00250 mol	+ 0.00250 mol	
Final	0.00250 mol	0	0.00250 mol	

Step 3: Determine equilibrium concentrations to find pH.

$$[CH_3COOH] = \frac{0.00250\ \text{mol}}{0.0625\ \text{L}} = 0.0400\ \text{M}$$
$$[CH_3COO^-] = \frac{0.00250\ \text{mol}}{0.0625\ \text{L}} = 0.0400\ \text{M}$$

Since the [base]/[acid] ratio is 1, pH = pK_a:

$$\text{pH} = pK_a + \log\frac{[\text{A}^-]}{[\text{HA}]} = -\log(1.8\times10^{-5}) + \log\frac{0.0400\ \text{M}}{0.0400\ \text{M}} = 4.74$$

This observation can be made by going through the ICE table process as well.

Overall, it is useful to remember that when you are halfway to the equivalence point of a weak acid titration pH = pK_a, and that you can apply this defintion without the need for these calculations each time.

4. At the equivalence point (adding 25.00 mL NaOH)

At the equivalence point, exactly enough base has been added to completely neutralize the acid and you are left with a salt solution:

Step 1: Find the moles of the acid and base:

$$\text{mol}_{CH_3COOH} = (0.100\ \frac{\text{mol}}{\text{L}})(0.05000\ \text{L}) = 0.00500\ \text{mol}$$

$$\text{mol}_{NaOH} = \text{mol}_{OH^-} = (0.200\ \frac{\text{mol}}{\text{L}})(0.0250\ \text{L}) = 0.00500\ \text{mol}$$

Step 2: Determine the moles of species after the neutralization reaction.

$CH_3COOH(aq)$ +	$OH^-(aq)$ ⇌	$CH_3COO^-(aq)$ +	$H_2O(l)$

Initial	0.00500 mol	0.00500 mol	0	X
Change	- 0.00500 mol	- 0.00500 mol	+ 0.00500 mol	
Final	0	0	0.00500 mol	

Step 3: Determine equilibrium concentrations to find pH.

$$[CH_3COO^-] = \frac{0.00500 \text{ mol}}{0.0750 \text{ L}} = 0.0667 \text{ M}$$

As discussed in section 9.1 the salt solution produced from the neutralization reaction of a weak acid and a strong base will be basic with the pH determined using the concentration of the weak conjugate base. At the endpoint of this neutralization reaction, the solution contains 0.0667 M CH_3COO^-:

	$CH_3COO^-(aq)$ +	$H_2O(l)$ ⇌	$CH_3COOH(aq)$ +	$OH^-(aq)$
Initial	0.0667 M	X	0	0
Change	- x		+ x	+ x
Equilibrium	0.0667 - x		x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{x^2}{0.0667 - x} = 5.6 \times 10^{-10}$$

Since K_b is very small, the base will only ionize slightly and we can assume that $x << 0.0667$ M.

$$K_b = \frac{x^2}{0.0667} = 5.6 \times 10^{-10}$$
$$x = 6.11 \times 10^{-6} \text{ M}$$

Checking assumption:

$$\frac{6.11 \times 10^{-6}}{0.0667} \times 100\% = 0.0092\% \text{ (valid)}$$

$$[OH^-] = 6.11 \times 10^{-6} \text{ M}$$

$$pOH = -\log[OH^-] = 5.21$$

$$pH = 14 - pOH = 8.79$$

5. After the equivalence point (adding 30.00 mL NaOH)

Past the equivalence point we are added a strong base to an already basic solution.

Step 1: Find the moles of the acid and base:

$$\text{mol}_{CH_3COOH} = (0.100 \frac{\text{mol}}{\text{L}})(0.05000 \text{ L}) = 0.00500 \text{ mol}$$

$$\text{mol}_{NaOH} = \text{mol}_{OH^-} = (0.200 \frac{\text{mol}}{\text{L}})(0.0300 \text{ L}) = 0.00600 \text{ mol}$$

Step 2: Determine the moles of species after the neutralization reaction.

	$CH_3COOH(aq)$ +	$OH^-(aq)$ ⇌	$CH_3COO^-(aq)$ +	$H_2O(l)$
Initial	0.00500 mol	0.00600 mol	0 M	X
Change	- 0.00500 mol	- 0.00500 mol	+ 0.00500 mol	
Final	0	0.00100 mol	0.00500 mol	

Step 3: Determine pH.

OH^- is present in excess. CH_3COO^- still acts as a weak base (as seen in the equivalence point calculation), but the OH^- produced from the ionization will be negligible compared to excess OH^- from the additional $NaOH$.

$$[OH^-] = \frac{0.00100 \text{ mol}}{0.0800 \text{ L}} = 0.0125 \text{ M}$$

$$pOH = -\log[OH^-] = 1.90$$

$$pH = 14 - pOH = 12.10$$

In general, the $[OH^-]$ formed from the ionization of the conjugate base is negligible beyond the equivalence point, and the pH can be determined by the excess $[OH^-]$ from the added $NaOH$.

Example 9.4.2

What is the pH of the solution after 20.00 mL of 0.200 M $NaOH$ is added to 50.00 mL of 0.100 M acetic acid (K_a = 1.8 x 10^{-5})?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Find the moles of $NaOH$ and CH_3COOH.
B. Write the neutralization reaction and determine the concentrations of species present after the reaction is complete.
C. Determine the pH either using the Henderson-Hasselbalch equation or an ICE table.

Solution

A. Find the moles of the acid and base:

$$\text{mol}_{CH_3COOH} = (0.100 \frac{\text{mol}}{\text{L}})(0.05000 \text{ L}) = 0.00500 \text{ mol}$$

$$\text{mol}_{NaOH} = \text{mol}_{OH^-} = (0.200 \frac{\text{mol}}{\text{L}})(0.02000L) = 0.00400\text{mol}$$

B. Determine the moles of each species after the neutralization reaction. Note that this reaction goes to completion due to the presence of a strong base:

	$CH_3COOH(aq)$ +	$OH^-(aq)$ ⇌	$CH_3COO^-(aq)$ +	$H_2O($
Initial	0.00500 mol	0.00400 mol	0 mol	X
Change	- 0.00400 mol	- 0.00400 mol	+ 0.00400 mol	
Final	0.00100 mol	0	0.00400 mol	

Calculate concentrations using the total volume (0.0500 L + 0.0200 L = 0.0700 L):

$$[CH_3COOH] = \frac{0.00100 \text{ mol}}{0.0700 \text{ L}} = 0.0143 \text{ M}$$
$$[CH_3COO^-] = \frac{0.00400 \text{ mol}}{0.0700 \text{ L}} = 0.0571 \text{ M}$$

C: Determine equilibrium concentrations to find pH:

	$CH_3COOH(aq)$ +	$H_2O(l)$ ⇌	$CH_3COO^-(aq)$ +	$H_3O^+(aq)$
Initial	0.0143 M	X	0.0571 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0143 M - x		0.0571 M + x	x

$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{(x)(0.0571+x)}{0.0143-x} = 1.8 \times 10^{-5}$

Since K_a is very small, the acid will only ionize slightly and we can assume that $x << 0.0143$ M.

$K_a = \frac{(x)(0.0571)}{0.0143} = 1.8 \times 10^{-5}$ $x = 4.51 \times 10^{-6}$ M

Checking assumption:

$\frac{4.51 \times 10^{-6}}{0.0143} \times 100\% = 0.0315\%$

The assumption is valid since the percentage is less than 5%.

$$[H_3O^+] = 4.51 \times 10^{-6} \text{ M}$$
$$\text{pH} = -\log[H_3O^+] = 5.35$$

The solution is still acidic (pH < 7) because a significant amount of the weak acid remains.

Alternatively, the Henderson-Hasselbalch equation can be used with the initial concentrations of CH_3COOH and CH_3COO^- after neutralization because the degree of ionization is small:

$$\text{pH} = pK_a + \log\frac{[A^-]}{[HA]} = -\log(1.8 \times 10^{-5}) + \log\frac{0.0571 \text{ M}}{0.0143 \text{ M}} = 5.36$$

Exercise 9.4.2

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer available at the end of this section.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, neutralization occurs in stages. The most acidic proton is titrated first, followed by the next most acidic, and so on. The titration curve shows distinct steps, each corresponding to the removal of a proton. A titration of the triprotic acid $\mathrm{H_3PO_4}$ with NaOH is illustrated in Figure 9.4.6 and shows two well-defined steps: the first midpoint corresponds to pK_{a1}, and the second midpoint corresponds to pK_{a2}. Because $\mathrm{HPO_4^{2-}}$ is such a weak acid, pK_{a3} has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant. Calculations with polyprotic acids are beyond the scope of CHM 135H.

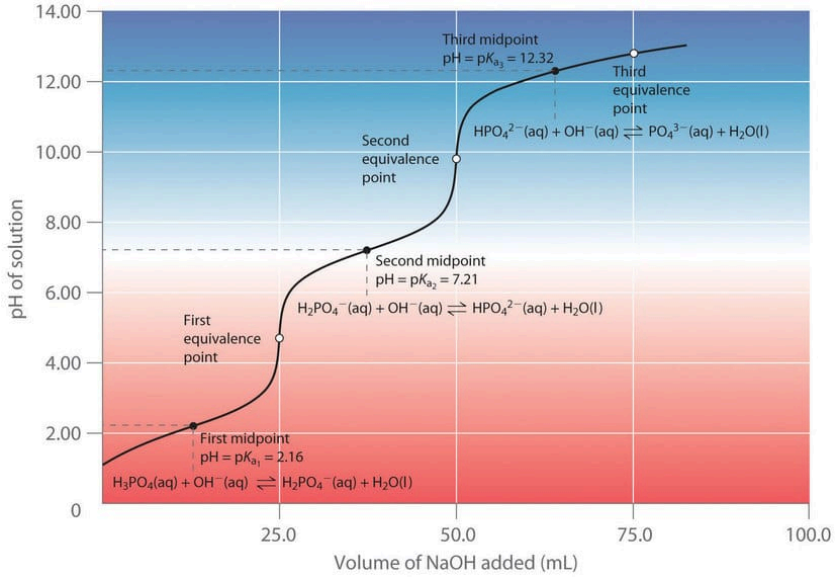


Figure 9.4.6: Titration Curve for Phosphoric Acid ($\mathrm{H_3PO_4}$), a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M $\mathrm{H_3PO_4}$ solution with 0.100 M NaOH along with the species in solution at each K_a is shown. Note the two distinct equivalence points corresponding to deprotonation of $\mathrm{H_3PO_4}$ at pH ≈ 4.6 and $\mathrm{H_2PO_4^{2-}}$ at pH ≈ 9.8. Because $\mathrm{HPO_4^{2-}}$ is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

Indicators

In most acid-base titrations, pH is not directly measured using a meter. Instead, an acid-base indicator is selected that undergoes a visible colour change at a pH close to the equivalence point.

Indicators are weak acids or bases with conjugate acid-base pairs that have distinctly different colours. The general reaction for an indicator (HIn) is:

$$\mathrm{HIn\,(aq)} \rightleftharpoons \mathrm{H^+\,(aq) + In^-\,(aq)}$$

where:

- HIn (protonated form) has one colour
- $\mathrm{In^-}$ (deprotonated form) has another colour.

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]}$$

The pK_{in} (the pK_a of the indicator) determines the pH at which the indicator changes colour. The pK_{in} of an indicator is the same as the pK_a of the indicator molecule: it is the pH at which $[\mathrm{In^-}]$ = $[\mathrm{HIn}]$, and the indicator appears as a colour mix of the two forms.

A good indicator for a titration should:

- Have a clear, easily detectable colour change
- Change colour rapidly near the equivalence point
- Not react with the substances in the titration
- Have a pK_{in} within one pH unit of the expected pH at the equivalence point

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure $9.4.7$ shows the approximate pH range over which some common indicators change colour and their change in colour. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change colour twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

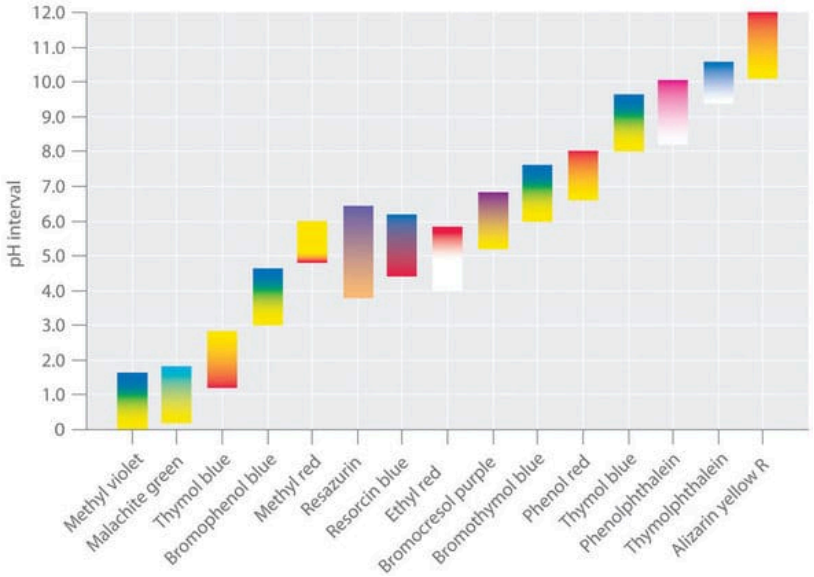


Figure $9.4.7$: Some Common Acid–Base Indicators. Approximate colours are shown, along with pK_{in} values and the pH range over which the colour changes. (CC BY-SA-NC; Anonymous by request)

For strong acid-strong base titrations, the pH changes sharply, so many indicators (e.g., methyl red, bromothymol blue, phenolphthalein) can be used. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors in detecting the equivalence point, as illustrated in Figure $9.4.8$. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M NaOH. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change colour are also shown. For the strong acid-strong base curve, both indicators change colour on the vertical part of the curve at 50 mL, so both would be suitable to indicate the equivalence point. For the weak acid-strong base titration curve, methyl red would change colour before the equivalence point, making it an unsuitable choice of indicator.

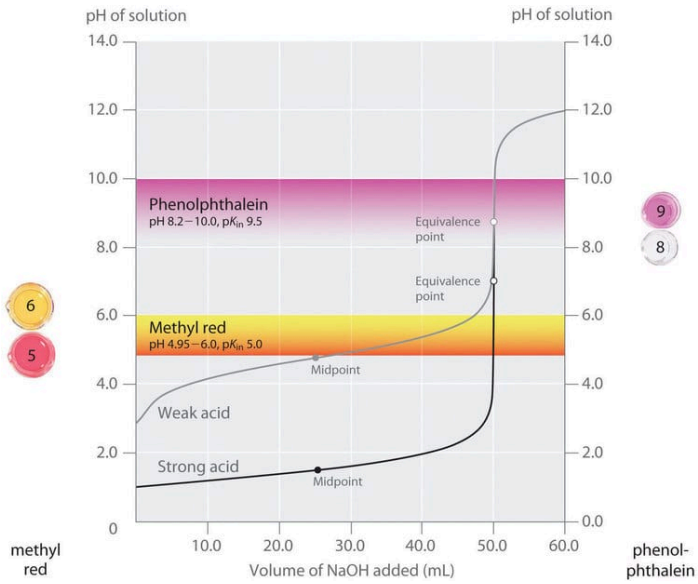


Figure 9.4.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

Methyl red is appropriate when the pH at the equivalence point is between 4.9 and 6.0. Phenolphthalein is appropriate for equivalence points between about 8.2 and 10.0.

The existence of many different indicators with different colours and pK_{in} values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as "pH paper," which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting colour with the standards printed on the container (Figure 9.4.9).

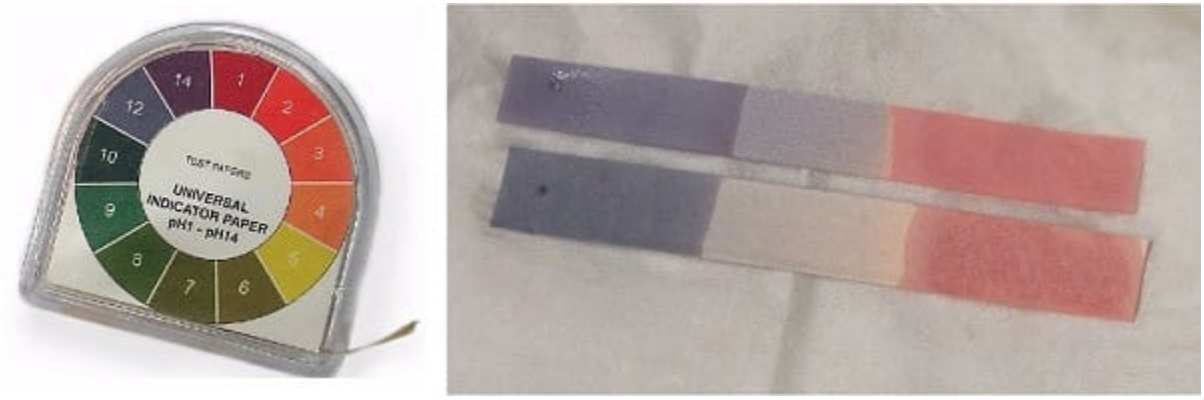


Figure 9.4.9: pH Paper. pH paper contains a set of indicators that change colour at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the colour to the standards provided. (CC BY-SA-NC; Anonymous by request)

Summary

Titration curves are plots of pH vs. volume of titrant added and provide valuable information about a titration. These curves can be used to determine concentrations of unknown solutions and the equilibrium constants for acid or base dissociation.

The equivalence point is where exactly enough acid or base has been added to completely react with the other component.

- For strong acid-strong base titrations, the equivalence point is at pH 7.0.
- For weak acid-strong base titrations, the equivalence point is above pH 7.
- For weak base-strong acid titrations, the equivalence point is below pH 7.

Titration curves for weak acids and weak bases vary significantly based on the identity of the compound.

Before the equivalence point, pH changes more gradually in weak acid and weak base titrations compared to strong acid-strong base titrations. This is due to the formation of a buffer consisting of a weak acid and its conjugate base (or vice versa for bases).

At the midpoint (halfway to the equivalence point), pH = pK_a for weak acids and pOH = pK_b for weak bases.

Acid-base indicators are weak acids or bases that change colour at a specific pH, corresponding to the protonation or deprotonation of the indicator molecule.

Glossary

acid-base titration curve
: The plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration.

endpoint
: The measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see equivalence point).

equivalence point
: The volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction.

midpoint
: The point on a titration curve halfway between start of the curve and the equivalence point, or between equivalence points in a polyprotic titration.

pH indicator
: An organic acid or base whose color changes depending on the pH of the solution it is in; permits visual detection of endpoint; also called acid-base indicator

Answers

Exercise 9.4.1

The neutralization reaction goes to completion. Find the moles of each reactant and determine which is in excess:

$$\text{mol}_{\text{NaOH}} = \text{mol}_{\text{OH}^-} = (0.133\ \frac{\text{mol}}{\text{L}})(0.07500\ \text{L}) = 0.009975\ \text{mol}$$

$$\text{mol}_{\text{HCl}} = \text{mol}_{\text{H}_3\text{O}^+} = (0.237\ \frac{\text{mol}}{\text{L}})(0.04000\ \text{L}) = 0.00948\ \text{mol}$$

	$\text{OH}^-\,(\text{aq}) +$	$\text{H}_3\text{O}^+\,(\text{aq})$ ⇌	$2\,\text{H}_2\text{O}\,(\text{l})$
Initial	0.009975 mol	0.00948 mol	X
Change	- 0.00948 mol	- 0.00948 mol	
Final	0.000495 mol	0	

OH^- is in excess. Find the $[\text{OH}^-]$ given the total volume (0.04000 L + 0.07500 L = 0.1150 L) of the solution:

$$[\text{OH}^-] = \frac{0.000495\ \text{mol}}{0.1150\ \text{L}} = 4.3 \times 10^{-3}\ \text{M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 2.37 \quad \text{pH} = 14 - \text{pOH} = 11.63$$

Exercise 9.4.2

A. Find the moles of the acid and base:

$$\text{mol}_{\text{NH}_3} = (0.150\ \frac{\text{mol}}{\text{L}})(0.1250\ \text{L}) = 0.01875\ \text{mol}$$

$$\text{mol}_{\text{HCl}} = \text{mol}_{\text{H}_3\text{O}^+} = (0.213\ \frac{\text{mol}}{\text{L}})(0.0450\ \text{L}) = 0.009585\ \text{mol}$$

B. Determine the moles of each species after the neutralization reaction. Note that this reaction goes to completion due to the presence of a strong base:

	$\text{NH}_3\,(\text{aq})\ +$	$\text{H}_3\text{O}^+\,(\text{aq})$ ⇌	$\text{NH}_4^+\,(\text{aq})\ +$	$\text{H}_2\text{O}\,(\text{l})$
Initial	0.01875 mol	0.009585 mol	0	X
Change	- 0.009585 mol	- 0.009585 mol	+ 0.009585 mol	
Final	0.009165 mol	0	0.009585 mol	

Calculate concentrations using the total volume (0.1250 L + 0.0450 L = 0.1700 L):

$$[\mathrm{NH_3}] = \frac{0.009165\ \mathrm{mol}}{0.1700\ \mathrm{L}} = 0.0539\ \mathrm{M}$$
$$[\mathrm{NH_4^+}] = \frac{0.009585\ \mathrm{mol}}{0.1700\ \mathrm{L}} = 0.0564\ \mathrm{M}$$

C: Determine equilibrium concentrations to find pH:

	$\mathrm{NH_4^+(aq)} +$	$\mathrm{H_2O(l)}$ ⇌	$\mathrm{NH_3(aq)} +$	$\mathrm{H_3O^+(aq)}$
Initial	0.0564 M	X	0.0539 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0564 M - x		0.0539 M + x	x

$$pK_b = 4.75 \quad K_b = 10^{-pK_b} = 1.78 \times 10^{-5}$$
$$K_a(\mathrm{NH_4^+}) = \frac{K_w}{K_b(\mathrm{NH_3})} = 5.62 \times 10^{-10}$$

$K_a = \frac{[\mathrm{NH_3}][\mathrm{H_3O^+}]}{[\mathrm{NH_4^+}]} = \frac{(x)(0.0539+x)}{0.0564-x} = 5.62 \times 10^{-10}$

Since K_a is very small, the acid will only ionize slightly and we can assume that \(\mathrm{x << 0.0538 ~\text{M}}\).

$K_a = \frac{(x)(0.0539)}{0.0564} = 5.62 \times 10^{-10}\ x = 5.88 \times 10^{-10}\ \mathrm{M}$

Checking assumption:

$\frac{5.88 \times 10^{-10}}{0.0539} \times 100\% = 1.1 \times 10^{-6}\%$

The assumption is valid since the percentage is less than 5%.

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 9.23$$

Alternatively, the Henderson-Hasselbalch equation can be used with the initial concentrations of $\mathrm{NH_4^+}$ and $\mathrm{NH_3}$ after neutralization:

$$\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = -\log(5.62 \times 10^{-10}) + \log\frac{0.0539\ \mathrm{M}}{0.0564\ \mathrm{M}} = 9.23$$

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9.5: Solubility Equilibria

Learning Objectives

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium calculations involving solubility, equilibrium expressions, and solute concentrations

Solubility equilibria occur when dissolution (solid dissolving into ions) and precipitation (ions forming a solid) happen at equal rates. Solubility equilibria play a role in important processes, such as tooth decay, water purification, and drug formulation. Understanding the factors that affect solubility helps in managing these processes effectively.

Solubility equilibria follow the same principles as other equilibrium systems, where the forward and reverse reactions occur at equal rates. The main difference is that solubility equilibria involve a solid dissolving into aqueous ions. Just like with chemical equilibria, we can use an equilibrium constant to describe the system and predict solubility under different conditions.

Compounds vary in their solubility. Highly soluble compounds dissolve completely in water, while sparingly soluble ones dissolve only slightly. Compounds that are considered insoluble have extremely low solubility in water.

When a substance is added to a solvent in excess, it may form a saturated solution, where an equilibrium is established between the dissolved and undissolved solute.

For example, in a saturated solution of silver chloride (AgCl), the following equilibrium is established (Figure $9.5.1$):

$$\mathrm{AgCl\,(s)} \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Ag^+\,(aq) + Cl^-\,(aq)}$$

- Solid AgCl dissolves to form aqueous $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$ ions.
- At the same time, these ions recombine and precipitate back into solid AgCl.
- Because AgCl is sparingly soluble, the equilibrium concentration of its dissolved ions in the solution is relatively low.

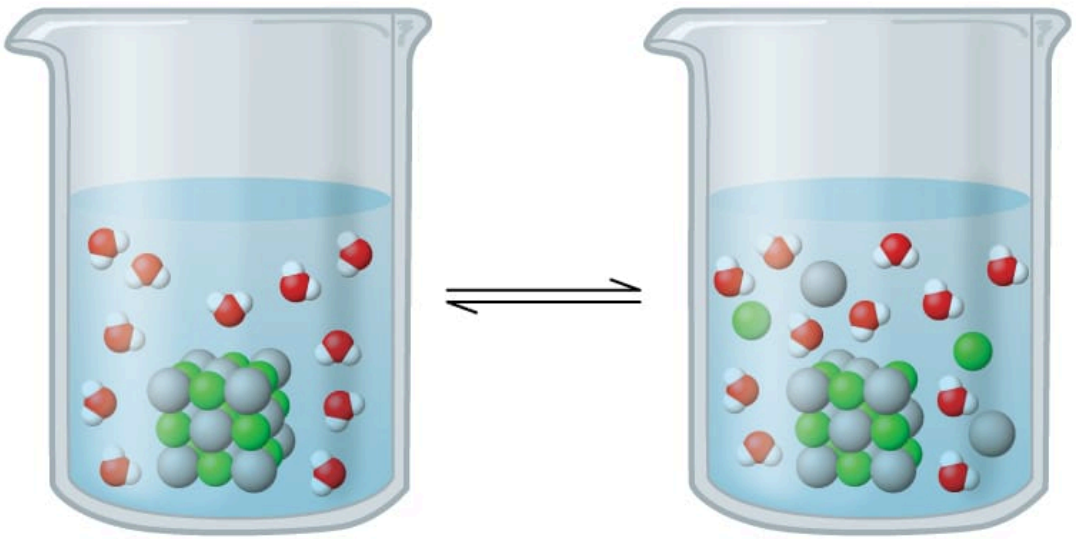


Figure $9.5.1$: Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture cons of a very dilute solution of $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$ ions in equilibrium with undissolved silver chloride.

Since solubility equilibria follow the same rules as other equilibrium systems, we can write an equilibrium expression for a dissolving solid, just as we do for gases or aqueous reactions. The equilibrium constant for a solubility equilibrium is called the solubility product constant (K_{sp}).

For silver chloride:

$$\mathrm{AgI(s)} \rightleftharpoons \mathrm{Ag^+(aq) + I^-(aq)} \quad K_{sp} = [\mathrm{Ag^+}][\mathrm{I^-}]$$

As with all equilibrium expressions, only gases and solutes appear in K_{sp} expressions. Solids are omitted because their activity is 1.

Example 9.5.1: Writing Equations and Solubility Products

Write the dissolution equation and the solubility product expression for each of the following slightly soluble ionic compounds:

a. AgI, silver iodide, a solid with antiseptic properties
b. $\mathrm{CaCO_3}$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids
c. $\mathrm{Mg(OH)_2}$, magnesium hydroxide, the active ingredient in Milk of Magnesia

Solution

a. $$\mathrm{AgI(s)} \rightleftharpoons \mathrm{Ag^+(aq) + I^-(aq)} \quad K_{sp} = [\mathrm{Ag^+}][\mathrm{I^-}]$$

b. $$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq) + CO_3{}^{2-}(aq)} \quad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{CO_3{}^{2-}}]$$

c. $$\mathrm{Mg(OH)_2(s)} \rightleftharpoons \mathrm{Mg^{2+}(aq) + 2\,OH^-(aq)} \quad K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}^2]$$

Exercise 9.5.1

Write the dissolution equation and the solubility product for each of the following slightly soluble compounds:

a. $\mathrm{BaSO_4}$
b. $\mathrm{Ag_2SO_4}$
c. $\mathrm{Al(OH)_3}$

Answer available at the end of this section.

K_{sp} and Solubility

The solubility product (K_{sp}) for a slightly soluble compound is determined experimentally by measuring how much compound dissolves in solution. Solubility can be expressed as the mass of solute that dissolves (typically in grams per 100 mL of solution), or as molar solubility (the number of moles of solute that dissolve per litre of solution). These values allow us to calculate K_{sp}, and vice versa, as illustrated in the next examples.

Example 9.5.2: Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, $\mathrm{CaF_2}$, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF_2(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq) + 2\,F^-(aq)}$$

Fluorite is added to water to give a saturated solution, in which the concentration of $\mathrm{Ca^{2+}}$ is measured to be 2.15×10^{-4} M. What is the solubility product, K_{sp}, of fluorite?

Solution

According to the stoichiometry of the dissolution equation, the fluoride ion molarity of a $\mathrm{CaF_2}$ solution is equal to twice its calcium ion molarity:

	$CaF_2(s)$ ⇌	$Ca^{2+}(aq)$ +	$2\,F^-(aq)$
Initial	X	0 M	0 M
Change		+ x	+ 2x
Equilibrium		x = 2.15 x 10^{-4} M	2x

$$[F^-] = (2x) = (2)(2.15 \times 10^{-4}\ \text{M}) = 4.30 \times 10^{-4}\ \text{M}$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2.15 \times 10^{-4})(4.30 \times 10^{-4})^2 = 3.98 \times 10^{-11}$$

Exercise 9.5.2

$Mg(OH)_2(s)$ is added to water to give a saturated solution in which the concentration of Mg^{2+} is measured to be 1.31×10^{-4} M. What is the solubility product (K_{sp}) for $Mg(OH)_2$?

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Answer available at the end of this section.

Example 9.5.3: Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The dissolution equation and solubility product expression are

$$CuBr(s) \rightleftharpoons Cu^+(aq)^+\ Br^-(aq)$$

with

$$K_{sp} = [Cu^+]\,[Br^-]$$

Following the ICE approach to this calculation yields the table

	CuBr (s) ⇌	Cu^+ (*aq*) +	Br^- (*aq*)
Initial concentration (*M*)		0	0
Change (*M*)		+*x*	+*x*
Equilibrium concentration (*M*)		*x*	*x*

Substituting the equilibrium concentration terms into the solubility product expression and solving for x yields

$$K_{sp} = [\mathrm{Cu^+}]\,[\mathrm{Br^-}]$$
$$6.3 \times 10^{-9} = (x)(x) = x^2$$
$$x = \sqrt{6.3 \times 10^{-9}}$$
$$= 7.9 \times 10^{-5}\,\mathrm{M}$$

The molar solubility of CuBr is 7.9×10^{-5} M.

Exercise 9.5.3

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer available at the end of this section.

Example 9.5.4: Determination of Molar Solubility from K_{sp}

The K_{sp} of calcium hydroxide, $\mathrm{Ca(OH)_2}$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$\mathrm{Ca(OH)_2\,(s)} \rightleftharpoons \mathrm{Ca^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

with

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{OH^-}]^2$$

The ICE table for this system is

	$\mathrm{Ca(OH)_2\,(s)} \rightleftharpoons$	$\mathrm{Ca^{2+}\,(aq)}$	+ $\mathrm{2OH^-\,(aq)}$
Initial concentration (*M*)		0	0
Change (*M*)		+*x*	+2*x*
Equilibrium concentration (*M*)		*x*	2*x*

Substituting terms for the equilibrium concentrations into the solubility product expression and solving for x gives

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{OH^-}]^2$$
$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)\left(4x^2\right) = 4x^3$$
$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}}$$
$$= 6.9 \times 10^{-3}\,\mathrm{M}$$

The molar solubility of $\mathrm{Ca(OH)_2}$ is 6.9×10^{-3} M.

Exercise 9.5.4

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer available at the end of this section.

Example 9.5.5: Determination of K_{sp} from Solubility in g/L

Many of pigments used in oil-based paints (Figure 9.5.2) are only sparingly soluble in water. For example, the solubility of chrome yellow, ($PbCrO_4$), an artist's pigment, is 4.6×10^{-6} g/L. Determine the solubility product (K_{sp}) for $PbCrO_4$.



Figure 9.5.2: Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

Before calculating the solubility product, the provided solubility must be converted to molarity:

$$[PbCrO_4] = \frac{4.6 \times 10^{-6} \text{ g PbCrO4}}{1 \text{ L}} \times \frac{\text{mol}}{323.2 \text{ g}}$$

$$= \frac{1.4 \times 10^{-8} \text{ mol } PbCrO_4}{1 \text{ L}}$$

$$= 1.4 \times 10^{-8} \text{ M}$$

	$PbCrO_4(s)$ ⇌	$Pb^{2+}(aq) +$	$CrO_4{}^{2-}(aq)$
Initial	X	0 M	0 M
Change		+ x	+ x
Equilibrium		x	x

The molar solubility (x) is 1.4×10^{-8} M, so:

$$K_{sp} = [Pb^{2+}][CrO_4{}^{2-}] = (1.4 \times 10^{-8} \text{ M})(1.4 \times 10^{-8} \text{ M}) = 2.0 \times 10^{-16}$$

Exercise 9.5.5

The solubility of thallium(I) chloride (TlCl), an intermediate formed during the isolation of thallium from ores, is 3.12 g/L at 20 °C. What is its solubility product (K_{sp})?

Answer available at the end of this section.

Chemistry is Everyday Life: Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique involves the ingestion of a barium compound before taking an X-ray image. Patients are given a chalky suspension of barium sulfate ($\mathrm{BaSO_4}$), which coats the lining of the digestive tract.

Because the K_{sp} of barium sulfate is very small (2.3×10^{-8}), only a tiny amount dissolves. This makes it safe to ingest and ensures that the compound remains mostly as a solid. On an X-ray, the barium-coated areas appear white, providing much more detail than a regular X-ray (Figure 9.5.3).



Figure 9.5.3: A suspension of barium sulfate coats the intestinal tract, permitting greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)

Doctors use this technique to help diagnose conditions such as acid reflux, Crohn's disease, and ulcers, among others.

Common Ion Effect

The solubility of an ionic compound is lower in a solution that already contains one of its ions than in pure water. This is another example of the common ion effect, a consequence of the law of mass action that can be explained using Le Châtelier's principle. For example, consider the dissolution of silver iodide:

$$\mathrm{AgI(s)} \rightleftharpoons \mathrm{Ag^+(aq) + I^-(aq)}$$

If additional $\mathrm{Ag^+}$ or $\mathrm{I^-}$ is added to the solution, the equilibrium shifts to the left. As a result, more AgI precipitates and the concentrations of dissolved $\mathrm{Ag^+}$ and $\mathrm{I^-}$ decrease. This means that less AgI dissolves in a solution already containing $\mathrm{Ag^+}$ or $\mathrm{I^-}$ than in pure water.

This effect can also be understood mathematically using the solubility product expression:

$$K_{sp} = [\mathrm{Ag^+}]\,[\mathrm{I^-}]$$

Since K_{sp} is constant at a given temperature, increasing the concentration of one ion requires the other to decrease to maintain equilibrium. This explains why adding a common ion reduces solubility.

Example 9.5.6: Common Ion Effect on Solubility

What is the effect on the amount of solid $\mathrm{Mg(OH)_2}$ and the concentrations of $\mathrm{Mg^{2+}}$ and $\mathrm{OH^-}$ when each of the following is added to a saturated solution of $\mathrm{Mg(OH)_2}$?

a. $\mathrm{MgCl_2}$
b. KOH
c. $\mathrm{NaNO_3}$
d. $\mathrm{Mg(OH)_2}$
e. HCl

Solution

The solubility equilibrium is

$$\mathrm{Mg(OH)_2\,(s)} \rightleftharpoons \mathrm{Mg^{2+}\,(aq)} + 2\,\mathrm{OH^-\,(aq)}$$

a. Adding a common ion, $\mathrm{Mg^{2+}}$, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of hydroxide ion and increasing the amount of undissolved magnesium hydroxide.
b. Adding a common ion, $\mathrm{OH^-}$, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of magnesium ion and increasing the amount of undissolved magnesium hydroxide.
c. The added compound does not contain a common ion, and has no effect on the magnesium hydroxide solubility equilibrium.
d. Adding more solid magnesium hydroxide will increase the amount of undissolved compound in the mixture. The solution is already saturated, though, so the concentrations of dissolved magnesium and hydroxide ions will remain the same.

$$Q = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q, and no shift is required to restore Q to the value of the equilibrium constant.
e. HCl would react with $\mathrm{OH^-}$, decreasing the $[\mathrm{OH^-}]$ which would shift the solubility equilibrium to the right, increasing the concentration of magnesium ion and decreasing the amount of undissolved magnesium hydroxide.

Exercise 9.5.6

What is the effect on the amount of solid $\mathrm{NiCO_3}$ and the concentrations of $\mathrm{Ni^{2+}}$ and $\mathrm{{CO_3}^{2-}}$ when each of the following are added to a saturated solution of $\mathrm{NiCO_3}$

a. $\mathrm{Ni(NO_3)_2}$
b. $\mathrm{KClO_4}$
c. $\mathrm{NiCO_3}$
d. $\mathrm{K_2CO_3}$

Answer available at the end of this section.

Example 9.5.7: Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010 M solution of cadmium bromide ($\mathrm{CdBr_2}$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

$$\mathrm{CdS\,(s)} \rightleftharpoons \mathrm{Cd^{2+}\,(aq)} + \mathrm{S^{2-}\,(aq)}$$

Cadmium bromide is a soluble salt that dissolves completely, contributing $Cd_2{}^+$ ions to the solution. So we start with an initial [$Cd_2{}^+$]=0.010 M before any CdS dissolves.

	$CdS\ (s) \rightleftharpoons Cd^{2+}\ (aq) + S^{2-}\ (aq)$		
Initial concentration (*M*)		0.010	0
Change (*M*)		+*x*	+*x*
Equilibrium concentration (*M*)		0.010 + *x*	*x*

$$K_{sp} = [Cd^{2+}][S^{2-}] = (0.010 + x)(x) = 1.0 \times 10^{-28}$$

Because K_{sp} is very small, assume $x \ll 0.010$ and solve the simplified equation for x:

$$(0.010)(x) = 1.0 \times 10^{-28} \tag{9.5.1}$$

$$x = 1.0 \times 10^{-26}\ \text{M}$$

The assumption is valid.

The molar solubility of CdS in this solution is 1.0×10^{-26} M.

Exercise 9.5.7

Calculate the molar solubility of aluminum hydroxide, $Al(OH)_3$, in a 0.015 M solution of aluminum nitrate, $Al(NO_3)_3$. The K_{sp} of $Al(OH)_3$ is 2×10^{-32}.

Answer available at the end of this section.

Summary

In a saturated solution, the undissolved solid is in equilibrium with its dissolved ions. The solubility product constant (K_{sp}) is the equilibrium constant for a dissolution reaction and reflects how much of a compound can dissolve in water.

The common ion effect occurs when a solution contains an ion that is also produced by the dissolution of a sparingly soluble salt. According to Le Châtelier's principle, this shifts the equilibrium to the left, decreasing solubility by increasing precipitation and lowering the concentration of dissolved ions.

Solubility equilibrium calculations allow us to determine K_{sp} from solubility data, or to calculate solubility from a known K_{sp}. These calculations help predict ion concentrations and understand how solubility changes under different conditions.

Glossary

dissolution
: The process by which solute components are dispersed in a solvent.

precipitation
: The process of dissolved ions in an aqueous solution reacting to form a solid precipitate.

solubility equilibrium
: Equilibrium established when dissolution of a dissolving solid and precipitation of its ions happen at equal rates.

solubility product constant (K_{sp})
The equilibrium constant for a solid substance dissolving in an aqueous solution.

Answers

Exercise 9.5.1

a. $\mathrm{BaSO_4(s)} \rightleftharpoons \mathrm{Ba^{2+}(aq) + SO_4{}^{2-}(aq)} \quad K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4{}^{2-}}]$

b. $\mathrm{Ag_2SO_4(s)} \rightleftharpoons \mathrm{2\,Ag^{+}(aq) + SO_4{}^{2-}(aq)} \quad K_{sp} = [\mathrm{Ag^{+}}]^2[\mathrm{SO_4{}^{2-}}]$

c. $\mathrm{Al(OH)_3(s)} \rightleftharpoons \mathrm{Al^{3+}(aq) + 3\,OH^{-}(aq)} \quad K_{sp} = [\mathrm{Al^{3+}}][\mathrm{OH^{-}}]^3$

Exercise 9.5.2

	$\mathrm{Mg(OH)_2(s)}$ ⇌	$\mathrm{Mg^{2+}(aq)}$ +	$\mathrm{2\,OH^{-}(aq)}$
Initial	X	0 M	0 M
Change		+ x	+ 2x
Equilibrium		x	2x

$$[\mathrm{OH^{-}}] = (2x) = (2)(1.31 \times 10^{-4}\ \mathrm{M}) = 2.62 \times 10^{-4}\ \mathrm{M}$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{OH^{-}}]^2 = (1.31 \times 10^{-4})(2.62 \times 10^{-4})^2 = 8.99 \times 10^{-12}$$

Exercise 9.5.3

	$\mathrm{AgI(s)}$ ⇌	$\mathrm{Ag^{+}(aq)}$ +	$\mathrm{I^{-}(aq)}$
Initial	X	0 M	0 M
Change		+ x	+ x
Equilibrium		x	x

$$\begin{aligned} K_{sp} &= [\mathrm{Ag^{+}}]\,[\mathrm{I^{-}}] \\ 1.5 \times 10^{-16} &= (x)(x) = x^2 \\ x &= \sqrt{1.5 \times 10^{-16}} \\ &= 1.2 \times 10^{-8}\ \mathrm{M} \end{aligned}$$

The molar solubility of AgI is 1.2×10^{-8} M.

Exercise 9.5.4

	$\mathrm{PbI_2(s)}$ ⇌	$\mathrm{Pb^{2+}(aq)}$ +	$\mathrm{2\,I^{-}(aq)}$
Initial	X	0 M	0 M
Change		+ x	+ 2x
Equilibrium		x	2x

$$\begin{aligned} K_{sp} &= [\mathrm{Pb^{2+}}][\mathrm{I^{-}}]^2 \\ 1.4 \times 10^{-8} &= (x)(2x)^2 = (x)\left(4x^2\right) = 4x^3 \\ x &= \sqrt[3]{\frac{1.4 \times 10^{-8}}{4}} \\ &= 1.5 \times 10^{-3}\ \mathrm{M} \end{aligned}$$

The molar solubility of $\mathrm{PbI_2}$ is 1.5×10^{-3} M

Exercise 9.5.5

	$\mathrm{TlCl(s)}$ ⇌	$\mathrm{Tl^{+}(aq)}$ +	$\mathrm{Cl^{-}(aq)}$
Initial	X	0 M	0 M
Change		+ x	+ x
Equilibrium		x	x

$$[\mathrm{TlCl}] = \frac{3.12\ \mathrm{g}}{\mathrm{L}}\left(\frac{\mathrm{mol}}{239.82\ \mathrm{g}}\right) = 0.0130\ \mathrm{M} = x$$

$$K_{sp} = [\mathrm{Tl^{+}}][\mathrm{Cl^{-}}] = (0.0130\ \mathrm{M})(0.0130\ \mathrm{M}) = 1.69 \times 10^{-4}$$

Exercise 9.5.6

(a) mass of $\mathrm{NiCO_3(s)}$ increases, $[\mathrm{Ni^{2+}}]$ increases, $\mathrm{CO_3}^{2-}$ decreases; (b) no effect; (c) no effect except to increase the amount of solid $\mathrm{NiCO_3}$; (d) mass of $\mathrm{NiCO_3(s)}$ increases, $[\mathrm{Ni^{2+}}]$ decreases, $\mathrm{CO_3}^{2-}$ increases;

Exercise 9.5.7

Aluminum nitrate dissolves completely in water, giving an initial $[\mathrm{Al^{3+}}]$ = 0.015M:

	$\mathrm{Al(OH)_3}$ ⇌	$\mathrm{Al^{3+}(aq)}$ +	$\mathrm{3\,OH^-(aq)}$
Initial	X	0.015 M	0 M
Change		+ x	+ 3x
Equilibrium		0.015 + x	3x

$$K_{sp} = [\mathrm{Al^{3+}}][\mathrm{OH^-}]^3 = (0.015 + x)(3x)^3 = 2 \times 10^{-32}$$

Assume $\mathrm{x} << 0.015\ \mathrm{M}$:

$$K_{sp} = (0.015)(3x)^3 = 2 \times 10^{-32}$$
$$x = 4 \times 10^{-11}\ \mathrm{M}$$

Assumption valid.

The molar solubility of $\mathrm{Al(OH)_3}$ in this solution is $4 \times 10^{-11}\ \mathrm{M}$.

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9.E: Applications of Aqueous Equilibria (Exercises)

Buffers

Exercise $9.E.1$*

What is the purpose of a buffer?

Answer available at the end of this section.

Exercise $9.E.2$*

How can a solution of sodium acetate, $\mathrm{NaCH_3COO}$, be converted into a buffer?

Answer available at the end of this section.

Exercise $9.E.3$**

Consider a buffer solution consisting of 1.0 M HX and 1.0 M $\mathrm{X^-}$. How will the following changes affect the pH of the solution?

a. Adding 0.1 M NaOH.

b. Adding 0.1 M HCl.

c. Adding additional HX.

d. Adding additional $\mathrm{X^-}$.

Answer available at the end of this section.

Exercise $9.E.4$**

What will be the pH of a buffer solution prepared from 0.20 mol $\mathrm{NH_3}$, 0.40 mol $\mathrm{NH_4NO_3}$, and just enough water to give 1.00 L of solution?

K_b for $\mathrm{NH_3}$ is 1.8 x 10^{-5}.

Answer available at the end of this section.

Exercise $9.E.5$***

A buffer solution is prepared from equal volumes of 0.200 M acetic acid ($\mathrm{CH_3COOH}$, K_a = 1.80 × 10^{-5}) and 0.600 M sodium acetate ($\mathrm{NaCH_3COO}$).

a. What is the pH of the solution?

b. Is the solution acidic or basic?

c. What is the pH of a solution that results when 3.00 mL of 0.340 M HCl is added to 0.200 L of the original buffer?

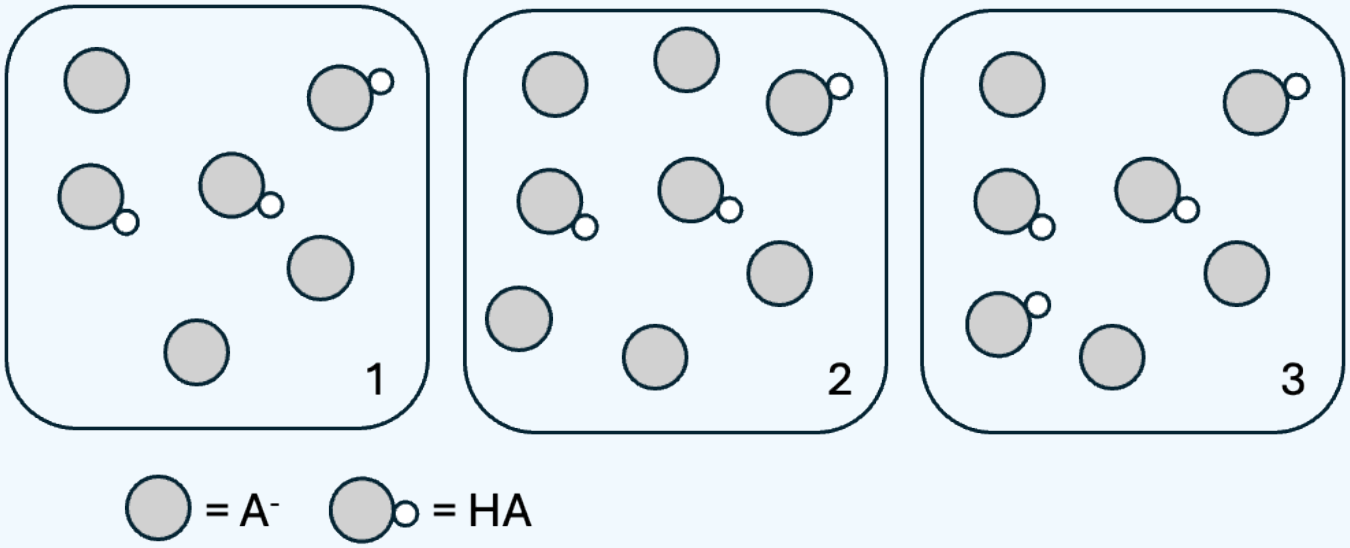
Answer available at the end of this section.

Exercise $9.E.6$*

The scenes below show three samples of a buffer containing the same weak acid (HA) and its conjugate base ($\mathrm{A^-}$). Other ions and water are omitted for clarity.

a. Which buffer has a pH equal to the pK_a of the weak acid?

b. Which buffer has the lowest pH?



Answer available at the end of this section.

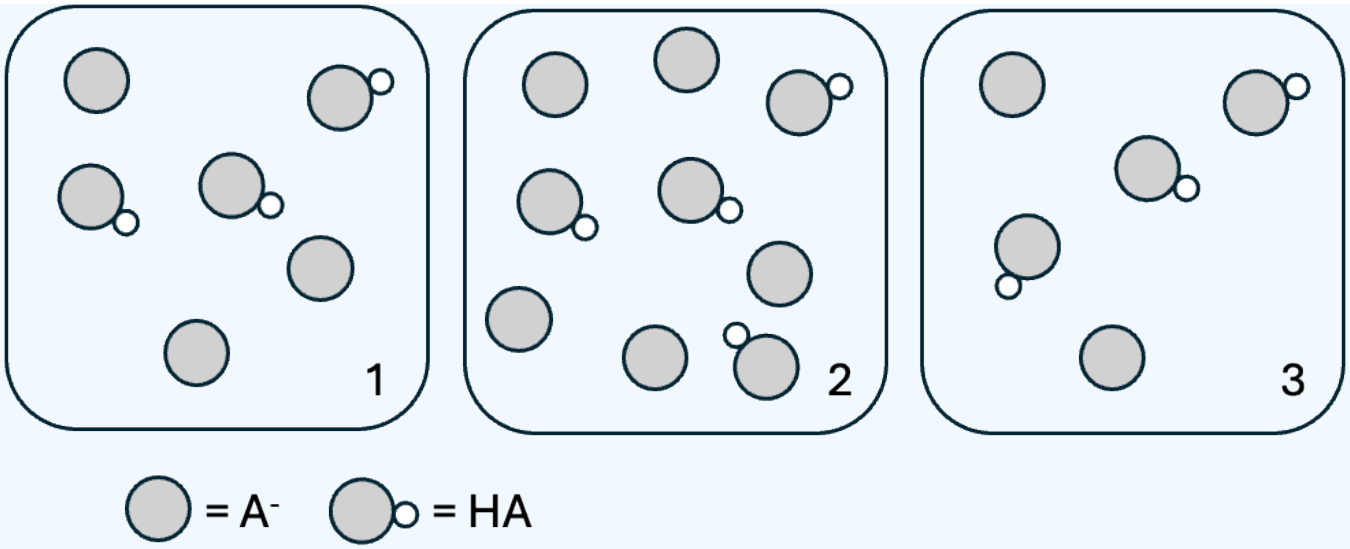
Example $9.E.7$**

HF (K_a = 6.2 x 10^{-4}) and NaF are used to make a buffer. You prepare 750 mL of a buffer solution containing 15 g of HF and 21 g of NaF. The molar masses of HF and NaF are 20 g/mol and 42 g/mol, respectively. What is the pH of the buffer?

Answer available at the end of this section.

Exercise $9.E.8$*

The scenes below show three samples of a buffer containing the same weak acid (HA) and conjugate base ($\mathrm{A^-}$). Other ions and water are omitted for clarity.



a. Order the buffers from lowest to highest pH.

b. Which buffer has the highest buffer capacity?

Answer available at the end of this section.

Exercise $9.E.9$***

a. What is the pH of a buffer consisting of 0.20 M HCN (K_a = 6.2 x 10^{-10}) and 0.10 M NaCN?

b. What is the pH after 0.020 mol of NaOH has been added to 0.500 L of the buffer (assume the volume remains constant)?

Answer available at the end of this section.

Exercise $9.E.10$*

Which of the following will produce a buffer solution? Explain your reasoning in each case.

a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride (NaF).
b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride (NaF).
c. mixing 100 mL of 0.1 M hydrofluoric acid (HF) and 100 mL of 0.1 M HCl.
d. mixing 100 mL of 0.1 M hydrofluoric acid (HF) and 50 mL of 0.1 M NaOH.
e. mixing 100 mL of 0.1 M sodium fluoride (NaF) and 50 mL of 0.1 M NaOH.

Answer available at the end of this section.

Exercise $9.E.11$*

You have been tasked with making a buffer with a pH of approximately 3.6. Which of the following acid–conjugate base pairs would be the best choice?

Acid	K_a

CH_3COOH	1.8×10^{-5}
$HClO$	4.0×10^{-8}
$HCOOH$	1.8×10^{-4}
HCN	6.2×10^{-10}
$HOBr$	2.3×10^{-9}

Answer available at the end of this section.

Acid-Base Titrations

Exercise $9.E.12$**

Predict whether each solution will be neutral, basic, or acidic at the equivalence point of each titration.

a. $NaOH\,(aq)$ is titrated with 0.100 M $HCl\,(aq)$
b. $CH_3CH_2NH_2\,(aq)$ is titrated with 0.150 M $HNO_3\,(aq)$
c. $HF\,(aq)$ is titrated with 0.100 M $NaOH\,(aq)$

Answer available at the end of this section.

Exercise $9.E.13$**

a. For the titration of any strong acid with any strong base, the pH at the equivalence point is 7.0. Why is this not the case in titrations of weak acids with strong bases?

b. Why are the titration curves for a strong acid with a strong base and a weak acid with a strong base identical in shape above the equivalence points but not below?

Answer available at the end of this section.

Exercise $9.E.14$**

A titration curve for a monoprotic weak acid titrated with a strong base can be divided into four distinct regions:

1. Initial Region: Before any base is added.
2. Midpoint Region
3. Equivalence Point
4. Post-Equivalence Region

Match each of the following descriptions to the appropriate region of the titration curve:

a. A buffer solution
b. A solution containing a weak base
c. A solution of a weak acid
d. A solution of strong base

Answer available at the end of this section.

Exercise $9.E.15$**

During the titration of a weak acid (e.g. acetic acid, $\mathrm{CH_3COOH}$) with a strong base (e.g. NaOH), what is the pH at each of the following stages along the titration curve? Rationalize the pH at each stage based on the species present.

a. At the beginning of the titration
b. At the midpoint of the titration
c. At the equivalence point
d. After the equivalence point

Answer available at the end of this section.

Exercise $9.E.16$**

During the titration of a weak base (e.g. ammonia, $\mathrm{NH_3}$) with a strong acid (e.g. HCl), what is the pH at each of the following stages along the titration curve? Rationalize the pH based on the species present.

a. At the beginning of the titration
b. At the midpoint of the titration
c. At the equivalence point
d. After the equivalence point

Answer available at the end of this section.

Exercise $9.E.17$***

What is the pH at each point during the titration of 20.00 mL of 0.200 M HCl with 0.200 M NaOH?

a. 0 mL b. 10.00 mL c. 19.00 mL d. 19.90 mL e. 20.00 mL f. 20.10 mL g. 30.00 mL

Answer available at the end of this section.

Exercise $9.E.18$***

What is the pH at each point during the titration of 40.0 mL of 0.100 M barbituric acid (K_a = 9.8 × 10^{-5}) with 0.100 M KOH?

a. 0 mL b. 20.0 mL c. 39.0 mL d. 40.0 mL e. 41.0 mL

Answer available at the end of this section.

Exercise $9.E.19$**

What volume of 0.350 M NaOH must be added to reach the equivalence point of the titrations with a) 50.0 mL of 0.100 M HCl and b) 50.0 mL of 0.100 M HCOOH (K_a = 1.78 x 10^{-4})? What is the pH at each equivalence point?

Answer available at the end of this section.

Exercise $9.E.20$***

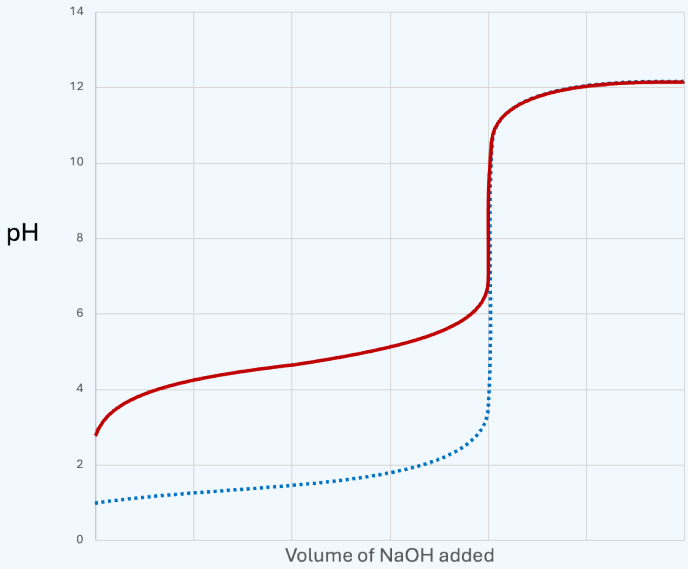
What is the pH at each point during the titration of 20.0 mL of 0.100 M ammonia (NH_3, K_b = 1.8 × 10^{-5}) with 0.200 M HCl?

a. 0 mL b. 5.0 mL c. 10.0 mL d. 15.0 mL

Answer available at the end of this section.

Exercise $9.E.21$**

Consider the following graph, which shows the titration of 20.0 mL of a monoprotic strong acid and 20.0 mL of a monoprotic weak acid with 0.100 M $NaOH$:



a. Which curve represents the strong acid?

b. Which of the two acids has the higher initial concentration?

c. Using Figure 8.3.7 (shown below), choose a suitable indicator for each titration.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

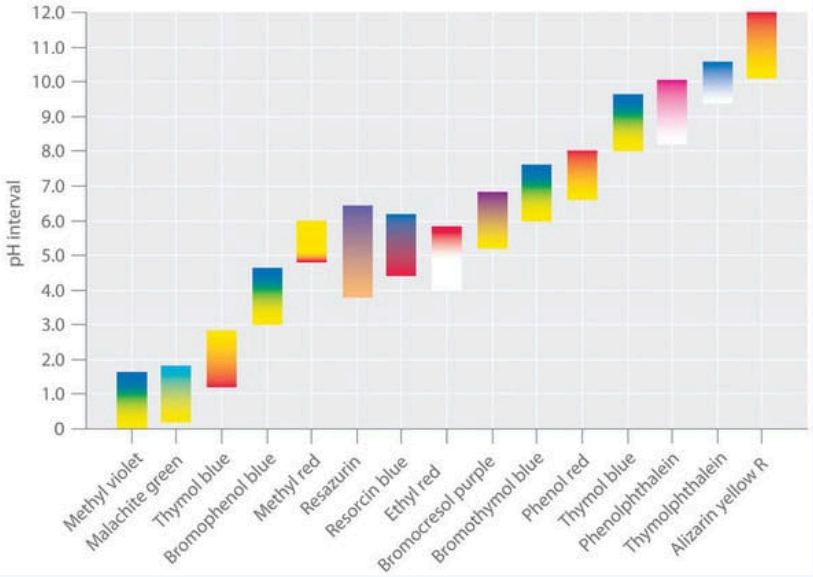


Figure 8.3.7: Some Common Acid–Base Indicators. Approximate colours are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

Answer available at the end of this section.

Exercise $9.E.22$**

The pK_a values of phenol red, bromophenol blue, and phenolphthalein are 7.4, 4.1, and 9.5, respectively. Which indicator is best suited for each acid–base titration?

a. $\mathrm{HNO_3\,(aq)}$ with $\mathrm{NaOH\,(aq)}$
b. $\mathrm{NH_3\,(aq)}$ with $\mathrm{HCl\,(aq)}$
c. $\mathrm{HClO_2\,(aq)}$ with $\mathrm{NaOH\,(aq)}$

Answer available at the end of this section.

Solubility Equilibria

Exercise $9.E.23$*

Write an expression for K_{sp} for each salt.

a. AgI
b. $\mathrm{CaF_2}$
c. $\mathrm{PbCl_2}$
d. $\mathrm{Ag_2CrO_4}$

Answer available at the end of this section.

Exercise $9.E.24$**

What is the molar solubility of each compound?

a. $\mathrm{BaCO_3}$ (K_{sp} = 2.6 x 10^{-9})
b. $\mathrm{BaF_2}$ (K_{sp} = 1.8 x 10^{-7})
c. $\mathrm{Ag_2CrO_4}$ (K_{sp} = 1.1 x 10^{-12})

Answer available at the end of this section.

Exercise $9.E.25$**

A student prepared 750 mL of a saturated solution of silver sulfate ($\mathrm{Ag_2SO_4}$). How many grams of $\mathrm{Ag_2SO_4}$ does the solution contain? K_{sp} = 1.20 × 10^{-5}.

Answer available at the end of this section.

Exercise $9.E.26$**

From the solubility data given, calculate K_{sp} for each compound.

a. AgI: 2.89 × 10^{-7} g/100 mL
b. $\mathrm{SrF_2}$: 1.22 × 10^{-2} g/100 mL
c. $\mathrm{Pb(OH)_2}$: 78 mg/500 mL

Answer available at the end of this section.

Exercise $9.E.27$**

You add 24.6 mg of barium sulfate ($\mathrm{BaSO_4}$) to 1.0 L of water at 25 °C and stir for several hours. After filtering and drying the remaining solid, you find that 22.1 mg did not dissolve. Based on your measurements, what is the K_{sp} of barium sulfate?

Answer available at the end of this section.

Exercise $9.E.28$**

Explain why the presence of $\mathrm{MgCl_2}$ decreases the molar solubility of the sparingly soluble salt $\mathrm{MgCO_3}$.

Answer available at the end of this section.

Exercise $9.E.29$***

What is the solubility of $\mathrm{BaCO_3}$ (K_{sp} = 2.58 x 10^{-9}) in pure water and in a 0.10 M $\mathrm{Na_2CO_3}$ solution?

Answer available at the end of this section.

Additional Problems

Exercise $9.E.30$**

Calcium hydroxide has a K_{sp} of 5.02 x 10^{-6}. What is the pH of a saturated solution of $\mathrm{Ca(OH)_2}$?

Answer available at the end of this section.

Exercise $9.E.31$**

What volume of 0.125 M HCl must be added to reach the equivalence point of the titration with 50.0 mL of 0.100 M methylamine ($\mathrm{CH_3NH_2}$, K_b = 4.6 x 10^{-4})? What is the pH at the equivalence point?

Answer available at the end of this section.

Exercise $9.E.32$**

In which solution will $\mathrm{CaCO_3\,(s)}$ be most soluble?

a. pure water b. 0.10 M $\mathrm{Na_2CO_3\,(aq)}$ c. 0.10 M $\mathrm{Ca(NO_3)_2\,(aq)}$ d. 0.10 M $\mathrm{HCl\,(aq)}$

Answer available at the end of this section.

Exercise $9.E.33$***

A buffer containing 0.100 M HA and 0.200 M NaA has a pH of 4.72. What is the pH after 10.0 mL of 0.100 M HCl is added to 250.0 mL of the buffer solution?

Answer available at the end of this section.

Answers

Exercise $9.E.1$*

A buffer resists pH changes upon the addition of an acid or base.

Exercise $9.E.2$*

A buffer solution consists of a weak acid and its conjugate base. In this case, acetate ($\mathrm{CH_3COO^-}$) is the conjugate base of acetic acid ($\mathrm{CH_3COOH}$). To form a buffer, we need both species in solution. This can be achieved in two ways:

1. Adding acetic acid ($\mathrm{CH_3COOH}$): Directly adding acetic acid to the sodium acetate solution provides both the weak acid and its conjugate base.
2. Adding a strong acid, such as hydrochloric acid (HCl): The strong acid ionizes to $\mathrm{H_3O^+}$, which reacts with some of the acetate ions to form acetic acid: $\mathrm{CH_3COO^-\,(aq) + H_3O^+\,(aq) \rightarrow CH_3COOH\,(aq) + H_2O\,(l)}$ Enough HCl would be added to react with about half of the acetate.

Both methods ensure that the solution contains a mixture of acetic acid and acetate, allowing it to resist changes in pH when small amounts of acid or base are added.

Exercise $9.E.3$**

The equilibrium reaction involved in the buffer is:

$\mathrm{HX\,(aq) + H_2O\,(l) \rightleftharpoons X^-\,(aq) + H_3O^+(\,aq)}$

a. The added NaOH is neutralized by HX:

$\mathrm{HX\,(aq) + OH^-\,(aq) \rightarrow X^-\,(aq) + H_2O\,(l)}$

leading to an increase in $[\mathrm{X^-}]$ and a decrease in $[\mathrm{HX}]$. This causes the equilibrium to shift left, decreasing the $[\mathrm{H_3O^+}]$ and resulting in a higher pH.

b. The added $\mathrm{H_3O^+}$ is neutralized by $\mathrm{X^-}$:

$\mathrm{X^-\,(aq) + H_3O^+\,(aq) \rightarrow HX\,(aq) + H_2O\,(l)}$

leading to an increase in $[\mathrm{HX}]$ and a decrease in $[\mathrm{X^-}]$. This causes the equilibrium to shift right, increasing the $[\mathrm{H_3O^+}]$ and resulting in a lower pH.

c. The additional HX causes the equilibrium to shift right, increasing the $[\mathrm{H_3O^+}]$ and resulting in a lower pH.

d. The additional $\mathrm{X^-}$ causes the equilibrium to shift left, decreasing the $[\mathrm{H_3O^+}]$ and resulting in a higher pH.

Exercise $9.E.4$**

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$pK_a = -\log K_a = 9.25$$

$$\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = 9.25 + \log\left(\frac{0.20\,\mathrm{M}}{0.40\,\mathrm{M}}\right) = 8.95$$

Exercise $9.E.5$***

a. pH can be found from an ICE table or the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log\frac{[\text{A}^-]}{[\text{HA}]} = -\log(1.80\times10^{-5}) + \log\left(\frac{0.600\,\text{M}}{0.200\,\text{M}}\right) = 5.222$$

b. The solution is acidic since the pH is less than 7.

c. Before considering the ionization equilibrium, the strong acid must be neutralized by the weak base. HCl is a strong acid and dissociates completely, contributing one mole of H_3O^+ per mole of HCl. Writing the neutralization reaction in terms of H_3O^+:

$$\text{CH}_3\text{COO}^-\,(\text{aq}) + \text{H}_3\text{O}^+\,(\text{aq}) \rightarrow \text{CH}_3\text{COOH}\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l})$$

The single reaction arrow indicates that this reaction goes to completion due to the presence of the strong acid.

First find the moles of all species:

$$\text{mol}_{\text{CH}_3\text{COOH}} = (0.200\ \frac{\text{mol}}{\text{L}})(0.200\,\text{L}) = 0.0400\,\text{mol}$$
$$\text{mol}_{\text{CH}_3\text{COO}^-} = (0.600\ \frac{\text{mol}}{\text{L}})(0.200\,\text{L}) = 0.120\,\text{mol}$$
$$\text{mol}_{\text{HCl}} = \text{mol}_{\text{H}_3\text{O}^+} = (0.340\ \frac{\text{mol}}{\text{L}})(0.00300\,\text{L}) = 0.00102\,\text{mol}$$

	$\text{CH}_3\text{COO}^-\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$ ⇌	$\text{CH}_3\text{COOH}\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$
Initial	0.120 mol	0.00102 mol	0.0400 mol	X
Change	- 0.00102 mol	- 0.00102 mol	+ 0.00102 mol	
Final	0.119 mol	0	0.0410 mol	

Now that all the strong acid (H_3O^+) has reacted, we consider the weak acid/base equilibrium between CH_3COOH and CH_3COO^- to determine the pH of the resulting buffer. The moles after the neutralization reaction can be used to find the initial concentrations in the ICE table (note: molarity, not moles, must be used in the ICE table). The total volume of the solution is 0.200 L (buffer solution) + 0.003 L (HCl) = 0.203 L

$$[\text{CH}_3\text{COO}^-] = \frac{0.119\,\text{mol}}{0.203\,\text{L}} = 0.586\,\text{M}$$
$$[\text{CH}_3\text{COOH}] = \frac{0.0410\,\text{mol}}{0.203\,\text{L}} = 0.202\,\text{M}$$

	$\text{CH}_3\text{COOH}\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$ ⇌	$\text{CH}_3\text{COO}^-\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$
Initial	0.202 M	X	0.586 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.202 - x		0.586 + x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(0.586+x)}{(0.202-x)} = 1.80\times10^{-5}$$

Since K_a is small, assume $\text{x} << 0.202$ and consequently $\text{x} << 0.586$ to simplify:

$$\frac{(x)(0.586)}{(0.202)} = 1.80\times10^{-5}$$
$$x = 6.20\times10^{-6}\ \text{M}$$

Check the assumption:

$$\frac{6.20\times10^{-6}\ \text{M}}{0.202\,\text{M}}\times100\% = 0.00307\%$$

Since it is less than 5%, the assumption is valid.

$$\begin{aligned}\text{pH} &= -\log\left[\text{H}_3\text{O}^+\right]\\ &= -\log\left(6.20\times10^{-6}\right)\\ &= 5.207\end{aligned}$$

OR use Henderson-Hasselbalch:

$$\text{pH} = pK_a + \log\frac{[\text{A}^-]}{[\text{HA}]} = -\log(1.80\times10^{-5}) + \log\left(\frac{0.586\,\text{M}}{0.202\,\text{M}}\right) = 5.207$$

Exercise $9.E.6$*

a. Buffer 1 has equal amounts of HA and A^-, so $[\text{HA}] = [\text{A}^-]$. This means pH = pK_a, according to the Henderson-Hasselbach equation.

b. Buffer 3 has more HA than A^-, so it has the lowest pH of the three samples.

A higher proportion of weak acid (HA) lowers the pH of a buffer, while a higher proportion of conjugate base (A^-) raises it.

Example $9.E.7$**

1. Calculate concentrations:

$$[\text{HF}] = \frac{15\,\text{g}\ \left(\frac{\text{mol}}{20\,\text{g}}\right)}{0.750\,\text{L}} = 1.0\ \text{M}$$
$$[\text{NaF}] = \frac{21\,\text{g}\ \left(\frac{\text{mol}}{42\,\text{g}}\right)}{0.750\,\text{L}} = 0.67\ \text{M}$$

2. Find pH through either ICE table or Henderson-Hasselbalch equation:

	$HF\,(aq)$ +	$H_2O\,(l)$ ⇌	$F^-\,(aq)$ +	$H_3O^+\,(aq)$
Initial	1.0 M	X	0.67 M	0 M
Change	- x		+ x	+ x
Equilibrium	1.0 - x		0.67 + x	x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(0.67+x)}{(1.0-x)} = 7.2\times10^{-4}$$

Since K_a is small, assume $x << 0.67$ and consequently $x << 1.0$ to simplify:

$$\frac{(x)(0.67)}{(1.0)} = 7.2\times10^{-4}$$
$$x = 1.1\times10^{-3}\ \text{M}$$

Check the assumption:

$$\frac{1.1\times10^{-3}\ \text{M}}{0.67\,\text{M}}\times100\% = 0.16\%$$

Since it is less than 5%, the assumption is valid.

$$\begin{aligned}\text{pH} &= -\log\left[H_3O^+\right]\\ &= -\log\left(1.1\times10^{-3}\right)\\ &= 2.97\end{aligned}$$

OR:

$$\text{pH} = pK_a + \log\frac{[A^-]}{[HA]} = -\log(7.2\times10^{-4}) + \log\left(\frac{0.67\,\text{M}}{1.0\,\text{M}}\right) = 2.97$$

Exercise $9.E.8$*

a. A higher proportion of weak acid (HA) lowers the pH of a buffer, while a higher proportion of conjugate base (A^-) raises it.

Buffer 1 has equal amounts of HA and A^-, so $[HA] = [A^-]$ and therefore pH = pK_a. Buffer 2 has $[HA] < [A^-]$ so pH > pK_a, and buffer 3 has $[HA] > [A^-]$, so pH < pK_a.

pH: 3 < 1 < 2

b. Buffer 2 has the highest concentration of acid and base, so it has the greatest buffer capacity.

Additional Information:
Buffer capacity depends not only on the total concentration of HA and A^-, but also on their ratio. A buffer resists changes from both added acid and base most effectively when $[HA] = [A^-]$, which corresponds to pH = pK_a. However, if one component is in excess, the buffer will be more effective against the opposite type of disturbance (e.g., more A^- gives greater resistance to added acid).

Exercise $9.E.9$***

a. To find the pH, we can either use an ICE table or the Henderson-Hasselbalch equation:

	$HCN\,(aq)$ +	$H_2O\,(l)$ ⇌	$CN^-\,(aq)$ +	$H_3O^+\,(aq)$
Initial	0.20 M	X	0.10 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.20 - x		0.10 + x	x

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(0.10+x)}{(0.20-x)} = 6.2\times10^{-10}$$

Since K_a is small, assume $x << 0.10$ and consequently $x << 0.20$ to simplify:

$$\frac{(x)(0.10)}{(0.20)} = 6.2\times10^{-10}$$
$$x = 1.24\times10^{-9}\ \text{M}$$

Check the assumption:

$$\frac{1.24\times10^{-9}\ \text{M}}{0.10\,\text{M}}\times100\% = 1.2\times10^{-6}\%$$

Since it is less than 5%, the assumption is valid.

$$\begin{aligned}\text{pH} &= -\log\left[H_3O^+\right]\\ &= -\log\left(1.2\times10^{-9}\right)\\ &= 8.91\end{aligned}$$

OR

$$\text{pH} = pK_a + \log\frac{[A^-]}{[HA]} = -\log(6.2\times10^{-10}) + \log\left(\frac{0.10\,\text{M}}{0.20\,\text{M}}\right) = 8.91$$

b. First consider the neutralization of the strong base.

$$\text{mol}_{\text{HCN}} = (0.20\ \frac{\text{mol}}{\text{L}})(0.500\ \text{L}) = 0.100\ \text{mol}$$
$$\text{mol}_{\text{CN}^-} = (0.10\ \frac{\text{mol}}{\text{L}})(0.500\ \text{L}) = 0.0500\ \text{mol}$$
$$\text{mol}_{\text{NaOH}} = \text{mol}_{\text{OH}^-} = 0.020\ \text{mol}$$

	$\text{HCN(aq)} +$	$\text{OH}^-\text{(aq)}$ ⇌	$\text{CN}^-\text{(aq)} +$	$\text{H}_2\text{O(l)}$
Initial	0.100 mol	0.020 mol	0.0500 mol	X
Change	- 0.020 mol	- 0.020 mol	+ 0.020 mol	
Final	0.080 mol	0	0.070 mol	

To find molarities, divide by the total volume (0.500 L):

$$[\text{HCN}] = \frac{0.080\ \text{mol}}{0.500\ \text{L}} = 0.16\ \text{M}$$
$$[\text{CN}^-] = \frac{0.070\ \text{mol}}{0.500\ \text{L}} = 0.14\ \text{M}$$

These concentrations are then the initial concentrations in the ICE table:

	$\text{HCN(aq)} +$	$\text{H}_2\text{O(l)}$ ⇌	$\text{CN}^-\text{(aq)} +$	$\text{H}_3\text{O}^+\text{(aq)}$
Initial	0.16 M	X	0.14 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.16 - x		0.14 + x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x)(0.14+x)}{(0.16-x)} = 6.2\times10^{-10}$$

Since K_a is small, assume $\text{x} << 0.14$ and consequently $\text{x} << 0.16$ to simplify:

$$\frac{(x)(0.14)}{(0.16)} = 6.2\times10^{-10}$$
$$x = 7.09\times10^{-10}\ \text{M}$$

Assumption valid.

$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log\left(7.09\times10^{-10}\right) \\ &= 9.15\end{aligned}$$

OR

$$\text{pH} = pK_a + \log\frac{[\text{A}^-]}{[\text{HA}]} = -\log(6.2\times10^{-10}) + \log\left(\frac{0.14\ \text{M}}{0.16\ \text{M}}\right) = 9.15$$

The addition of the strong base increased the pH from 8.91 (part a) to 9.15.

Exercise $9.E.10$*****

a. This will not produce a buffer solution because the hydrochloric acid completely reacts with the sodium fluoride to give sodium chloride and hydrofluoric acid.

b. This will produce a buffer solution because the hydrochloric acid reacts with half of the NaF to produce HF and NaCl. The solution then consists of a weak acid and its conjugate base.

c. This will not produce a buffer solution because hydrofluoric acid is a weak acid and hydrochloric acid is a strong acid.

d. This will produce a buffer solution because NaOH reacts with half of the HF to produce NaF and H_2O. The solution then consists of a weak acid and its conjugate base.

e. This will not produce a buffer solution because sodium fluoride is a weak base and sodium hydroxide is a strong base.

Exercise $9.E.11$*****

To form a buffer with a specific pH, we choose a conjugate acid–base pair where the pK_a is close to the desired pH. This ensures that $[\text{HA}]\approx[\text{A}^-]$, and the buffer will resist pH changes effectively.

Calculate pK_a values for each acid:

Acid	K_a	pK_a
CH_3COOH	1.8×10^{-5}	4.74
HClO	4.0×10^{-8}	7.40
HCOOH	1.8×10^{-4}	3.74
HCN	6.2×10^{-10}	9.21
HOBr	2.3×10^{-9}	8.64

HCOOH/NaHCOO would be the best choice since its pK_a is closest to 3.6.

Exercise $9.E.12$******

a. The solution will be neutral at the equivalence point because sodium hydroxide is a strong base and hydrochloric acid is a strong acid:

$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$

NaCl is a neutral salt.

b. The solution will be acidic at the equivalence point because ethylamine is a weak base and nitric acid is a strong acid. At the equivalence point, $\mathrm{CH_3CH_2NH_3^+}$, a weak acid, is present:

$\mathrm{CH_3CH_2NH_2\ (aq) + HNO_3\ (aq) \rightarrow CH_3CH_2NH_3^+\ (aq) + NO_3^-\ (aq) + H_2O\ (l)}$ $\mathrm{CH_3CH_2NH_3^+\ (aq) + H_2O\ (l) \rightleftharpoons CH_3CH_2NH_2\ (aq) + H_3O^+\ (aq)}$

The formation of $\mathrm{H_3O^+}$ leads to an acidic solution.

c. The solution will be basic at the equivalence point because HF is a weak acid and NaOH is a strong base. At the equivalence point, $\mathrm{F^-}$, a weak base, is present:

$\mathrm{HF\ (aq) + OH^-\ (aq) \rightarrow F^-\ (aq) + H_2O\ (l)}$ $\mathrm{F^-\ (aq) + H_2O\ (l) \rightleftharpoons HF\ (aq) + OH^-\ (aq)}$

The formation of $\mathrm{OH^-}$ leads to a basic solution.

Exercise $9.E.13$**

a. At the equivalence point of a titration, all of the acid has reacted with the base. This leaves only the conjugate base ($\mathrm{X^-}$) of the acid in solution. If HA is a weak acid, its conjugate base $\mathrm{A^-}$ can act as a weak base and react with water to form $\mathrm{OH^-}$, making the solution basic:

$\mathrm{HX\ (aq) + OH^-\ (aq) \rightarrow X^-\ (aq) + H_2O\ (l)}$ $\mathrm{X^-\ (aq) + H_2O\ (l) \rightleftharpoons HX\ (aq) + OH^-\ (aq)}$

For a strong acid, however, its conjugate base is so weak that it does not react with water, so the solution remains neutral and the pH at the equivalence point is 7.

b. The titration curves for a strong acid with a strong base and a weak acid with a strong base look the same above the equivalence point because both involve adding excess strong base. The strong base completely neutralizes the acid and dominates the solution, making it strongly basic. Below the equivalence point, the weak acid only partially ionizes, creating a buffer region and a gradual increase in pH. A strong acid, by contrast, ionizes completely, producing a sharper pH rise.

Exercise $9.E.14$**

a. A buffer solution exists around the midpoint of the titration. The midpoint of the titration is defined as the point at which exactly enough acid or base has been added to neutralize one-half of the acid originally present. At this point, the solution contains equal amounts of the weak acid and conjugate base, effectively resisting changes in pH.

b. At the equivalence point, the amount of titrant added is enough to completely react with the weak acid, resulting in a solution containing only the conjugate base of the weak acid, which is itself a weak base.

c. Initially, the solution consists of a weak acid before any titration is added. The pH is higher than a strong acid of the same concentration but lower than 7.

d. After the equivalence point, excess strong base is present.

Exercise $9.E.15$**

a. **At the beginning of the titration**

The initial pH is determined by the weak acid's partial ionization in water. For acetic acid:

$$\mathrm{CH_3\ CO_2\ H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3\ COO^-(aq)}$$

The pH is less than 7. The pH for a weak acid is higher than for a strong acid of the same concentration.

b. **At the midpoint of the titration**

The midpoint of the titration is defined as the point at which exactly enough base has been added to neutralize one-half of the acid originally present:

$$\mathrm{CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)}$$

pH = pK_a since $\mathrm{[CH_3COOH] = [CH_3COO^-]}$.

The pH begins to increase, but the presence of both acid and conjugate base creates a buffer that resists large changes in pH. This continues until the strong base has overcome the buffer capacity.

c. **At the equivalence point**

At the equivalence point, the amount of titrant added is enough to completely react with the weak acid, resulting in a solution composed of the conjugate base (a weak base):

$$\mathrm{CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)}$$

The pH is greater than 7 because of the presence of the conjugate base which forms some $\mathrm{OH^-}$:

$$\mathrm{CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)}$$

d. **After the equivalence point**

The pH is greater than 7 and determined by the concentration of excess NaOH added.

Exercise $9.E.16$**

a. **At the beginning of the titration**

The initial pH is determined by the partial ionization of the weak base in water:

$$\mathrm{NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4{}^+(aq)}$$

The pH is greater than 7 due to the production of $\mathrm{OH^-}$. However, because $\mathrm{NH_3}$ is a weak base, the pH is lower than that of a strong base at the same concentration.

b. **At the midpoint of the titration**

At the midpoint, exactly half of the $\mathrm{NH_3}$ has reacted with the added HCl, forming an equal amount of $\mathrm{NH_4{}^+}$:

$$\mathrm{NH_3(aq) + H_3O^+(aq) \rightarrow NH_4{}^+(aq) + H_2O(l)}$$

pH = pK_a since $\mathrm{[NH_3] = [NH_4{}^+]}$.

The pH drops gradually as acid is added, but the buffer resists large changes until the buffer capacity is surpassed.

c. **At the equivalence point**

At this point, all of the $\mathrm{NH_3}$ has reacted with HCl, leaving a solution of $\mathrm{NH_4{}^+}$, a weak acid:

$$\mathrm{NH_3(aq) + H_3O^+(aq) \rightarrow NH_4{}^+(aq) + H_2O(l)}$$

The pH is less than 7 because of the presence of the conjugate base, which forms \(\ce{H3O+}\):

$$\mathrm{NH_4{}^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)}$$

d. **After the equivalence point**

Beyond this point, an excess strong acid has been added. The pH is determined entirely by the concentration of excess H_3O^+ from the strong acid. pH < 7.

Exercise $9.E.17$***

Since HCl is a strong acid, it ionizes completely, so $[HCl] = [H_3O^+]$.

a. $[HCl] = [H_3O^+] = 0.200\ M$; $pH = -\log[H_3O^+] = 0.699$

b. Find the moles of each reactant:

$$mol_{NaOH} = mol_{OH^-} = (0.200\ \frac{mol}{L})(0.01000\,L) = 0.00200\,mol$$
$$mol_{HCl} = mol_{H_3O^+} = (0.200\ \frac{mol}{L})(0.02000\,L) = 0.00400\,mol$$

	$OH^-(aq) +$	$H_3O^+(aq)$ ⇌	$2\,H_2O(l)$
Initial	0.00200 mol	0.00400 mol	X
Change	- 0.00200 mol	- 0.00200 mol	
Final	0	0.00200 mol	

H_3O^+ is in excess. Find the $[H_3O^+]$ given the total volume (0.0200 L + 0.0100 L = 0.0300 L) of the solution:

$$[H_3O^+] = \frac{0.00200\,mol}{0.0300\,L} = 0.0667\,M$$
$$pH = -\log[H_3O^+] = 1.176$$

c. Find the moles of each reactant:

$$mol_{NaOH} = mol_{OH^-} = (0.200\ \frac{mol}{L})(0.01900\,L) = 0.00380\,mol$$
$$mol_{HCl} = mol_{H_3O^+} = (0.200\ \frac{mol}{L})(0.02000\,L) = 0.00400\,mol$$

	$OH^-(aq) +$	$H_3O^+(aq)$ ⇌	$2\,H_2O(l)$
Initial	0.00380 mol	0.00400 mol	X
Change	- 0.00380 mol	- 0.00380 mol	
Final	0	0.00020 mol	

H_3O^+ is in excess. Find the $[H_3O^+]$ given the total volume (0.0200 L + 0.0190 L = 0.0390 L) of the solution:

$$[H_3O^+] = \frac{0.00020\,mol}{0.0390\,L} = 0.00513\,M$$
$$pH = -\log[H_3O^+] = 2.289$$

d. Find the moles of each reactant:

$$mol_{NaOH} = mol_{OH^-} = (0.200\ \frac{mol}{L})(0.01990\,L) = 0.00398\,mol$$
$$mol_{HCl} = mol_{H_3O^+} = (0.200\ \frac{mol}{L})(0.02000\,L) = 0.00400\,mol$$

	$OH^-(aq) +$	$H_3O^+(aq)$ ⇌	$2\,H_2O(l)$
Initial	0.00398 mol	0.00400 mol	X
Change	- 0.00398 mol	- 0.00398 mol	
Final	0	0.00002 mol	

H_3O^+ is in excess. Find the $[H_3O^+]$ given the total volume (0.0200 L + 0.0199 L = 0.0399 L) of the solution:

$$[H_3O^+] = \frac{0.00002\,mol}{0.0399\,L} = 0.000501\,M$$
$$pH = -\log[H_3O^+] = 3.300$$

e. Find the moles of each reactant:

$$mol_{NaOH} = mol_{OH^-} = (0.200\ \frac{mol}{L})(0.03000\,L) = 0.00400\,mol$$
$$mol_{HCl} = mol_{H_3O^+} = (0.200\ \frac{mol}{L})(0.02000\,L) = 0.00400\,mol$$

	$OH^-(aq) +$	$H_3O^+(aq)$ ⇌	$2\,H_2O(l)$
Initial	0.00400 mol	0.00400 mol	X
Change	- 0.00400 mol	- 0.00400 mol	
Final	0	0	

Since the moles of acid are equal to the moles of base, the equivalence point has been reached, and the pH is 7.

f. Find the moles of each reactant:

$$\text{mol}_{\text{NaOH}} = \text{mol}_{\text{OH}^-} = (0.200\ \frac{\text{mol}}{\text{L}})(0.02010\ \text{L}) = 0.00402\ \text{mol}$$
$$\text{mol}_{\text{HCl}} = \text{mol}_{\text{H}_3\text{O}^+} = (0.200\ \frac{\text{mol}}{\text{L}})(0.02000\ \text{L}) = 0.00400\ \text{mol}$$

	$OH^-(aq)$ +	$H_3O^+(aq)$ ⇌	$2\,H_2O(l)$
Initial	0.00402 mol	0.00400 mol	X
Change	- 0.00400 mol	- 0.00400 mol	
Final	0.00002 mol	0	

OH^- is now in excess.

$$[OH^-] = \frac{0.00002\ \text{mol}}{0.04010\ \text{L}} = 0.000499\ \text{M}$$
$$\text{pOH} = 3.302;\ \text{pH} = 10.698$$

g. Find the moles of each reactant:

$$\text{mol}_{\text{NaOH}} = \text{mol}_{\text{OH}^-} = (0.200\ \frac{\text{mol}}{\text{L}})(0.03000\ \text{L}) = 0.00600\ \text{mol}$$
$$\text{mol}_{\text{HCl}} = \text{mol}_{\text{H}_3\text{O}^+} = (0.200\ \frac{\text{mol}}{\text{L}})(0.02000\ \text{L}) = 0.00400\ \text{mol}$$

	$OH^-(aq)$ +	$H_3O^+(aq)$ ⇌	$2\,H_2O(l)$
Initial	0.00600 mol	0.00400 mol	X
Change	- 0.00400 mol	- 0.00400 mol	
Final	0.00200 mol	0	

$$[OH^-] = \frac{0.00200\ \text{mol}}{0.0500\ \text{L}} = 0.0400\ \text{M}$$
$$\text{pOH} = 1.398;\ \text{pH} = 12.602$$

Exercise $9.E.18$***

Let's write barbituric acid as HB for simplicity.

a.

	$HB(aq)$ +	$H_2O(l)$ ⇌	$B^-(aq)$ +	$H_3O^+(aq)$
Initial	0.100 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.100 M - x		x	x

$$K_a = \frac{[H_3O^+][B^-]}{[HB]} = \frac{x^2}{(0.100 - x)} = 9.8 \times 10^{-5}$$

Since K_a is small, assume $x << 0.100$ to simplify:

$$\frac{x^2}{(0.100)} = 9.8 \times 10^{-5}$$
$$x = 3.1 \times 10^{-3}\ \text{M}$$

Check the assumption:

$$\frac{3.1 \times 10^{-3}\ \text{M}}{0.100\ \text{M}} \times 100\% = 3.1\%$$

Since it is less than 5%, the assumption is valid.

$$\begin{aligned}\text{pH} &= -\log\left[H_3O^+\right] \\ &= -\log\left(3.1 \times 10^{-3}\right) \\ &= 2.50\end{aligned}$$

b. Once KOH is added, we need to consider neutralization and then equilibrium. Find the moles of the acid and base:

$$\text{mol}_{\text{HB}} = (0.100\ \frac{\text{mol}}{\text{L}})(0.04000\ \text{L}) = 0.00400\ \text{mol}$$
$$[\text{KOH}] = [OH^-] = (0.100\ \frac{\text{mol}}{\text{L}})(0.00200\ \text{L}) = 0.00200\ \text{mol}$$

	$HB(aq)$ +	$OH^-(aq)$ ⇌	$B^-(aq)$ +	$H_2O(l)$
Initial	0.00400 mol	0.00200 mol	0	X
Change	- 0.00200 mol	- 0.00200 mol	+ 0.00200 mol	
Final	0.00200 mol	0	0.00200 mol	

Calculate concentrations using the total volume (0.0400 L + 0.0020 L = 0.0600 L):

$$[\mathrm{HB}] = \frac{0.00200\,\mathrm{mol}}{0.0600\,\mathrm{L}} = 0.0333\,\mathrm{M}$$
$$[\mathrm{B^-}] = \frac{0.00200\,\mathrm{mol}}{0.0600\,\mathrm{L}} = 0.0333\,\mathrm{M}$$

To find pH, we can use either an ICE table with the final concentrations from the table above as the initial concentrations or use the Henderson-Hasselbalch equation:

$$\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = -\log\left(9.8\times10^{-5}\right) + \log\left(\frac{0.0333\ \mathrm{M}}{0.0333\ \mathrm{M}}\right) = 4.01$$

c. Find the moles of the acid and base:

$$\mathrm{mol_{HB}} = (0.100\ \frac{\mathrm{mol}}{\mathrm{L}})(0.04000\,\mathrm{L}) = 0.00400\,\mathrm{mol}$$
$$[\mathrm{NaOH}] = [\mathrm{OH^-}] = (0.100\ \frac{\mathrm{mol}}{\mathrm{L}})(0.00390\,\mathrm{L}) = 0.003900\,\mathrm{mol}$$

	$\mathrm{HB\,(aq)}$ +	$\mathrm{OH^-\,(aq)}$ ⇌	$\mathrm{B^-\,(aq)}$ +	$\mathrm{H_2O\,(l)}$
Initial	0.00400 mol	0.00390 mol	0	X
Change	- 0.00390 mol	- 0.00390 mol	+ 0.00390 mol	
Final	0.00010 mol	0	0.00390 mol	

Calculate concentrations using the total volume (0.0400 L + 0.0039 L = 0.0790 L):

$$[\mathrm{HB}] = \frac{0.00010\,\mathrm{mol}}{0.0790\,\mathrm{L}} = 0.00127\,\mathrm{M}$$
$$[\mathrm{B^-}] = \frac{0.00390\,\mathrm{mol}}{0.0790\,\mathrm{L}} = 0.0494\,\mathrm{M}$$

To find pH, we can use either an ICE table with the final concentrations from the table above as the initial concentrations or use the Henderson-Hasselbalch equation:

$$\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = -\log\left(9.8\times10^{-5}\right) + \log\left(\frac{0.0494\,\mathrm{M}}{0.00127\,\mathrm{M}}\right) = 5.60$$

d. Find the moles of the acid and base:

$$\mathrm{mol_{HB}} = (0.100\ \frac{\mathrm{mol}}{\mathrm{L}})(0.04000\,\mathrm{L}) = 0.00400\,\mathrm{mol}$$
$$[\mathrm{NaOH}] = [\mathrm{OH^-}] = (0.100\ \frac{\mathrm{mol}}{\mathrm{L}})(0.00400\,\mathrm{L}) = 0.004000\,\mathrm{mol}$$

This is the equivalence point - enough base has been added to neutralize all of the acid.

	$\mathrm{HB\,(aq)}$ +	$\mathrm{OH^-\,(aq)}$ ⇌	$\mathrm{B^-\,(aq)}$ +	$\mathrm{H_2O\,(l)}$
Initial	0.00400 mol	0.00400 mol	0	X
Change	- 0.00400 mol	- 0.00400 mol	+ 0.00400 mol	
Final	0	0	0.00400 mol	

Calculate concentrations using the total volume (0.0400 L + 0.0400 L = 0.0800 L):

$$[\mathrm{B^-}] = \frac{0.00400\,\mathrm{mol}}{0.0800\,\mathrm{L}} = 0.0500\,\mathrm{M}$$

While the weak acid and strong base have reacted completely, the conjugate base of the weak acid affects the pH at the equivalence point:

	$\mathrm{B^-\,(aq)}$ +	$\mathrm{H_2O\,(l)}$ ⇌	$\mathrm{HB\,(aq)}$ +	$\mathrm{OH^-\,(aq)}$
Initial	0.0500 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0500- x		x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{9.8\times10^{-5}} = \frac{[\mathrm{HB}][\mathrm{OH^-}]}{[\mathrm{B^-}]} = \frac{x^2}{0.0500-x} = 1.0\times10^{-10}$$

Since K_b is very small, the base will only ionize slightly, and we can assume that $x << 0.0500$ M.

$$K_b = \frac{x^2}{0.0500} = 1.0\times10^{-10}$$
$$x = 2.26\times10^{-6}\ \mathrm{M}$$

Checking the assumption:

\[\frac{2.26 \times 10^{-6}}{0.0500\,\text{M}} \times 100\% = 0.0045\% \] (valid)

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = 5.65;\ \mathrm{pH} = 14 - \mathrm{pOH} = 8.35$$

e. Find the moles of the acid and base:

$$\text{mol}_{\text{HB}} = (0.100\ \frac{\text{mol}}{\text{L}})(0.04000\,\text{L}) = 0.00400\,\text{mol}$$

$$[\text{NaOH}] = [\text{OH}^-] = (0.100\ \frac{\text{mol}}{\text{L}})(0.00410\,\text{L}) = 0.004100\,\text{mol}$$

This is past the equivalence point - excess strong base is present.

	HB(aq) +	$\text{OH}^-\text{(aq)}$ ⇌	$\text{B}^-\text{(aq)}$ +	$\text{H}_2\text{O(l)}$
Initial	0.00400 mol	0.00410 mol	0	X
Change	- 0.00400 mol	- 0.00400 mol	+ 0.00400 mol	
Final	0	0.00010 mol	0.00400 mol	

In this case, OH^- is present in excess. B^- still acts as a weak base (as seen in the equivalence point calculation), but the OH^- produced from the ionization of B^- will be negligible compared to the excess OH^-.

Calculate concentrations using the total volume (0.0400 L + 0.0410 L = 0.0810 L):

$$[\text{OH}^-] = \frac{0.00010\,\text{mol}}{0.0810\,\text{L}} = 0.00123\,\text{M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 2.91;\ \text{pH} = 11.09$$

Exercise $9.E.19$**

At the equivalence point enough base has been added to neutralize all of the acid:

$$\text{HX(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{X}^-\text{(aq)} + \text{H}_2\text{O(l)}$$

a. moles NaOH = moles HCl

$$\text{mol}_{\text{HCl}} = 0.100\ \tfrac{\text{mol}}{\text{L}}(0.0500\ \text{L}) = 0.00500\ \text{mol} = \text{mol}_{\text{NaOH}}\ \frac{0.00500\,\text{mol}}{0.350\ \tfrac{\text{mol}}{\text{L}}} = 0.0143\ \text{L}$$

Since Cl^- is a very weak base (conjugate base of a strong acid), the pH at the equivalence point is 7.

b. Since the volume and concentration of the HCOOH is the same as for HCl, the volume is the same:

moles NaOH = moles HCOOH

$$\text{mol}_{\text{HCOOH}} = 0.100\ \tfrac{\text{mol}}{\text{L}}(0.0500\ \text{L}) = 0.00500\ \text{mol} = \text{mol}_{\text{NaOH}}\ \frac{0.00500\,\text{mol}}{0.350\ \tfrac{\text{mol}}{\text{L}}} = 0.0143\ \text{L}$$

To find the pH, we need the concentration of the conjugate base, HCOO^-, present. For each mole of HCOOH that reacts, one mole of base forms:

$$\text{HCOOH(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{HCOO}^-\text{(aq)} + \text{H}_2\text{O(l)}$$

$$[\text{HCOO}^-] = \frac{\text{mol}}{\text{total volume}} = \frac{0.00500\,\text{mol}}{0.0643\,\text{L}} = 0.0778\ \text{M}$$

	$\text{HCOO}^-\text{(aq)}$ +	$\text{H}_2\text{O(l)}$ ⇌	HCOOH(aq) +	$\text{OH}^-\text{(aq)}$
Initial	0.0778 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0778 - x		x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.78\times10^{-4}} = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{x^2}{0.0778-x} = 5.62\times10^{-11}$$

Since K_b is very small, the base will only ionize slightly and we can assume that $x << 0.0778$ M.

$$K_b = \frac{x^2}{0.0778} = 5.62\times10^{-11}\ x = 2.09\times10^{-6}\ \text{M}$$

Checking assumption:

$$\frac{2.09\times10^{-6}}{0.0778\ \text{M}}\times100\% = 0.00269\%\ \text{(valid)}$$

$$\text{pOH} = -\log[\text{OH}^-] = 5.680;\ \ \text{pH} = 8.320$$

Exercise $9.E.20$***

a.

	$\text{NH}_3\text{(aq)}$ +	$\text{H}_2\text{O(l)}$ ⇌	$\text{NH}_4^+\text{(aq)}$ +	$\text{OH}^-\text{(aq)}$
Initial	0.100 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.100 - x		x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{(0.100-x)} = 1.8\times10^{-5}$$

Since K_b is very small, the base will only ionize slightly, and we can assume that $x << 0.100$ M.

$$K_b = \frac{x^2}{0.100} = 1.8\times10^{-5}$$
$$x = 1.34\times10^{-3}$$

Checking assumption:

$$\frac{1.34 \times 10^{-3}}{0.100} \times 100\% = 1.34\%$$

The assumption is valid since the percentage is less than 5%.

$$\text{pOH} = -\log\left[\text{OH}^-\right] = 2.87;\ \text{pH} = 11.13$$

b. Find the moles of the acid and base:

$$\text{mol}_{\text{NH}_3} = (0.100\ \frac{\text{mol}}{\text{L}})(0.0200\,\text{L}) = 0.00200\,\text{mol}$$

$$[\text{HCl}] = [\text{H}_3\text{O}^+] = (0.200\ \frac{\text{mol}}{\text{L}})(0.0050\,\text{L}) = 0.0010\,\text{mol}$$

Determine the moles of each species after the neutralization reaction. Note that this reaction goes to completion due to the presence of a strong acid:

	$\text{NH}_3\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$ ⇌	$\text{NH}_4{}^+\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$
Initial	0.00200 mol	0.0010 mol	0	X
Change	- 0.0010 mol	- 0.0010 mol	+ 0.0010 mol	
Final	0.0010 mol	0	0.0010 mol	

Calculate concentrations using the total volume (0.0200 L + 0.0050 L = 0.0250 L):

$$[\text{NH}_3] = \frac{0.0010\,\text{mol}}{0.0250\,\text{L}} = 0.0400\,\text{M}$$

$$[\text{NH}_4{}^+] = \frac{0.00100\,\text{mol}}{0.0250\,\text{L}} = 0.0400\,\text{M}$$

This is the halfway to the equivalence point where half of the NH_3 has been neutralized, so pH = pK_a:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$pK_a = -logK_a = 9.25$$

$$\text{pH} = pK_a + \log\frac{[\text{A}^-]}{[\text{HA}]} = 9.25 + \log\left(\frac{0.0400\,\text{M}}{0.0400\,\text{M}}\right) = 9.25$$

The pH could have also been found using an ICE table.

c. Find the moles of the acid and base:

$$\text{mol}_{\text{NH}_3} = (0.100\ \frac{\text{mol}}{\text{L}})(0.0200\,\text{L}) = 0.00200\,\text{mol}$$

$$[\text{HCl}] = [\text{H}_3\text{O}^+] = (0.200\ \frac{\text{mol}}{\text{L}})(0.0100\,\text{L}) = 0.00200\,\text{mol}$$

Determine the moles of each species after the neutralization reaction. Note that this reaction goes to completion due to the presence of a strong acid:

	$\text{NH}_3\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$ ⇌	$\text{NH}_4{}^+\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$
Initial	0.00200 mol	0.00200 mol	0	X
Change	- 0.00200 mol	- 0.00200 mol	+ 0.00200 mol	
Final	0	0	0.00200 mol	

It is the equivalence point! The NH_3 has completely reacted with the added acid, leaving $\text{NH}_4{}^+$:

Calculate concentrations using the total volume (0.0200 L + 0.0100 L = 0.0300 L):

$$[\text{NH}_4{}^+] = \frac{0.00200\,\text{mol}}{0.0300\,\text{L}} = 0.0667\,\text{M}$$

	$\text{NH}_4{}^+\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$ ⇌	$\text{NH}_3\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$
Initial	0.0667 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0667 - x		x	x

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4{}^+]} = \frac{x^2}{0.0667 - x} = 5.6 \times 10^{-10}$$

Since K_a is very small, the acid will only ionize slightly and we can assume that $\text{x} << 0.0667\ \text{M}$.

$$K_a = \frac{x^2}{0.0667} = 5.6 \times 10^{-10}$$

$$x = 6.1 \times 10^{-6}\ \text{M}$$

Checking assumption:

$$\frac{6.1 \times 10^{-6}}{0.0667} \times 100\% = 0.0091\%$$

The assumption is valid since the percentage is less than 5%.

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 5.21$$

d. Find the moles of the acid and base:

$$\text{mol}_{\text{NH}_3} = (0.100\ \frac{\text{mol}}{\text{L}})(0.0200\,\text{L}) = 0.00200\,\text{mol}$$

$$[\text{HCl}] = [\text{H}_3\text{O}^+] = (0.200\ \frac{\text{mol}}{\text{L}})(0.0150\,\text{L}) = 0.00300\,\text{mol}$$

Determine the moles of each species after the neutralization reaction. Note that this reaction goes to completion due to the presence of a strong acid:

	$\text{NH}_3\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$ ⇌	$\text{NH}_4^+\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$
Initial	0.00200 mol	0.00300 mol	0	X
Change	- 0.00200 mol	- 0.00200 mol	+ 0.00200 mol	
Final	0	0.00100 mol	0.00200 mol	

The acid is now in excess. NH_4^+ still acts as a weak acid (as seen in the equivalence point calculation), but the H_3O^+ produced from the ionization will be negligible compared to the excess strong acid.

Calculate concentrations using the total volume (0.0200 L + 0.0150 L = 0.0350 L):

$$[\text{H}_3\text{O}^+] = \frac{0.00100\,\text{mol}}{0.0350\,\text{L}} = 0.0286\,\text{M}$$

We can find the pH:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 1.544$$

Exercise $9.E.21$**

a. The blue dotted line represents the strong acid.
This is evident from the shape of the titration curve: the strong acid starts at a lower initial pH and shows a very sharp and steep rise in pH near the equivalence point. This steep jump is characteristic of strong acid–strong base titrations, because strong acids fully ionize, leading to a very low initial pH and no buffering before neutralization. The weak acid curve rises more gradually and has a noticeable buffer region before the equivalence point due to the presence of both HA and A^-.

b. Both acids have the same initial concentration.
This is because they both require the same volume of 0.100 M NaOH to reach the equivalence point. Since they are monoprotic acids, and neutralization is a 1:1 mole ratio, the moles of acid must be the same and since the volumes of the acid samples are equal, they must have the same molarity.

c. Indicator choice depends on the pH at the equivalence point. A good indicator changes colour in the steepest part of the titration curve near the equivalence point.

For the strong acid, the pH at the equivalence point is 7. The pH rises very steeply through this region, so many indicators would work. A good choice is bromothymol blue, which changes colour around pH 6.0–7.6, closely matching the steep portion of the curve.

For the weak acid, the pH at the equivalence point is above 7, typically in the 8–10 range. The pH rise near the equivalence point is more gradual, so it's important to choose an indicator that changes colour in that basic range. Suitable choices include phenolphthalein (colour change from pH 8.3 to 10.0) or thymol blue (second transition from pH 8.0 to 9.6).

Exercise $9.E.22$**

a. The titration of a strong acid with a strong base will have a pH of 7 at the equivalence point, so phenol red with the $pK_a = 7.4$ is best suited for the reaction.

b. At the equivalence point, NH_4^+ is present and acts as a weak acid, giving a pH of less than 7. Bromophenol blue with the $pK_a = 4.1$ is best suited for the reaction.

c. HClO_2 is a weak acid. At the equivalence point, ClO_2^- acts as a weak base giving a pH greater than 7. Phenolphthalein, with $pK_a = 9.5$, is best suited for the reaction.

Exercise $9.E.23$*

a. $\text{AgI}\,(\text{s}) \rightleftharpoons \text{Ag}^+\,(\text{aq}) + \text{I}^-\,(\text{aq})$
$K_{sp} = [\text{Ag}^+][\text{I}^-]$
b. $\text{CaF}_2\,(\text{s}) \rightleftharpoons \text{Ca}^{2+}\,(\text{aq}) + 2\,\text{F}^-\,(\text{aq})$
$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$
c. $\text{PbCl}_2\,(\text{s}) \rightleftharpoons \text{Pb}^{2+}\,(\text{aq}) + 2\,\text{Cl}^-\,(\text{aq})$
$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$
d. $\text{Ag}_2\text{CrO}_4\,(\text{s}) \rightleftharpoons 2\,\text{Ag}^+\,(\text{aq}) + \text{CrO}_4{}^{2-}\,(\text{aq})$
$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4{}^{2-}]$

Exercise $9.E.24$**

a.

	$\text{BaCO}_3\,(\text{s})$ ⇌	$\text{Ba}^{2+}\,(\text{aq})$ +	$\text{CO}_3{}^{2-}\,(\text{aq})$
Initial	X	0 M	0 M
Change		+ x	+ x
Equilibrium		x	x

$$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3{}^{2-}] = (x)(x) = 2.6 \times 10^{-9}\ x = 5.1 \times 10^{-5}\ \frac{\text{mol}}{\text{L}}$$

b.

$\text{BaF}_2\,(\text{s})$ ⇌	$\text{Ba}^{2+}\,(\text{aq})$ +	$2\,\text{F}^-\,(\text{aq})$

Initial	X	0 M	0 M
Change		+ x	+ 2x
Equilibrium		x	2x

$K_{sp} = [Ba^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3 = 1.8 \times 10^{-7}$ $x = 3.6 \times 10^{-3}$ $\frac{mol}{L}$

c.

	$Ag_2CrO_4(s)$ ⇌	$2\,Ag^+(aq)$ +	$CrO_4{}^{2-}(aq)$
Initial	X	0 M	0 M
Change		+ 2x	+ x
Equilibrium		2x	x

$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}] = (2x)^2(x) = 4x^3 = 1.1 \times 10^{-12}$ $x = 6.5 \times 10^{-5}$ $\frac{mol}{L}$

Exercise $9.E.25$**

	$Ag_2SO_4(s)$ ⇌	$2\,Ag^+(aq)$ +	$SO_4{}^{2-}(aq)$
Initial	X	0 M	0 M
Change		+ 2x	+ x
Equilibrium		2x	x

$K_{sp} = [Ag^+]^2[SO_4{}^{2-}] = (2x)^2(x) = 1.20 \times 10^{-5}$ $x = 0.0144$ $\frac{mol}{L}$

The molar mass of Ag_2SO_4 is 311.8 g/mol.

$0.0144\ \frac{mol}{L}(0.750\ L)(311.8\ \frac{g}{mol}) = 3.37\ g$

Exercise $9.E.26$**

a.

	$AgI(s)$ ⇌	$Ag^+(aq)$ +	$I^-(aq)$
Initial	X	0 M	0 M
Change		+ x	+ x
Equilibrium		x	x

$[Ag^+] = [I^-] = x = \frac{2.89 \times 10^{-7}\ g}{0.100\,L}\left(\frac{mol}{234.77\,g}\right) = 1.23 \times 10^{-8}\ M$

$K_{sp} = [Ag^+][I^-] = x^2 = 1.51 \times 10^{-16}$

b.

	$SrF_2(s)$ ⇌	$Sr^{2+}(aq)$ +	$2\,F^-(aq)$
Initial	X	0 M	0 M
Change		+ x	+ 2x
Equilibrium		x	2x

$x = \frac{1.22 \times 10^{-2}\ g}{0.100\,L}\left(\frac{mol}{125.62\,g}\right) = 9.71 \times 10^{-4}\ M$

$K_{sp} = [Sr^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3 = 4(9.71 \times 10^{-4})^3 = 3.66 \times 10^{-9}$

c.

	$Pb(OH)_2(s)$ ⇌	$Pb^{2+}(aq)$ +	$2\,OH^-(aq)$
Initial	X	0 M	0 M
Change		+ x	+ 2x
Equilibrium		x	2x

$x = \frac{0.078\,g}{0.500\,L}\left(\frac{mol}{241.21\,g}\right) = 6.47 \times 10^{-4}\ M$

$K_{sp} = [Pb^{2+}][OH^-]^2 = 4x^3 = 4(6.47 \times 10^{-4})^3 = 1.1 \times 10^{-9}$

Exercise $9.E.27$**

	$BaSO_4(s)$ ⇌	$Ba^{2+}(aq)$ +	$SO_4{}^{2-}(aq)$

Initial	X	0 M	0 M
Change		+ x	+ x
Equilibrium		x	x

$(24.6\text{ mg} - 22.1\text{ mg}) \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mol}}{233.38\text{ g}} \times \frac{1}{1.0\text{ L}} = 1.07 \times 10^{-5}\text{ M}$

$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4{}^{2-}] = x^2 = (1.07 \times 10^{-5}\text{ M})^2 = 1.15 \times 10^{-10}$

Exercise $9.E.28$**

$\text{MgCO}_3\,(\text{s}) \rightleftharpoons \text{Mg}^{2+}\,(\text{aq}) + \text{CO}_3{}^{2-}$

Adding a soluble Mg^{2+} salt increases $[\text{Mg}^{2+}]$ in solution. According to Le Châtelier's principle, this shift in concentration causes the equilibrium to shift to the left, decreasing the solubility of MgCO_3. This phenomenon is known as the common ion effect.

Exercise $9.E.29$***

Pure water:

	$\text{BaCO}_3\,(\text{s})$ ⇌	$\text{Ba}^{2+}\,(\text{aq})$ +	$\text{CO}_3{}^{2-}\,(\text{aq})$
Initial	X	0 M	0 M
Change		+ x	+ x
Equilibrium		x	x

$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3{}^{2-}] = (x)(x) = 2.58 \times 10^{-9}\ x = 5.08 \times 10^{-5}\text{ M}$

0.10 M Na_2CO_3:

	$\text{BaCO}_3\,(\text{s})$ ⇌	$\text{Ba}^{2+}\,(\text{aq})$ +	$\text{CO}_3{}^{2-}\,(\text{aq})$
Initial	X	0 M	0.10 M
Change		+ x	+ x
Equilibrium		x	0.10 + x

$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3{}^{2-}] = (x)(0.10 + x) = 2.58 \times 10^{-9}$

Assume x << 0.10, so $(x)(0.10) = 2.58 \times 10^{-9}$

This gives $x = 2.58 \times 10^{-8}\text{ M}$ and so the assumption is valid.

Exercise $9.E.30$**

To find the pH, we need to find the $[\text{OH}^-]$ dissolved in solution:

	$\text{Ca(OH)}_2\,(\text{s})$ ⇌	$\text{Ca}^{2+}\,(\text{aq})$ +	$2\,\text{OH}^-\,(\text{aq})$
Initial	X	0 M	0 M
Change		+ x	+ 2x
Equilibrium		x	2x

$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = (x)(2x)^2 = 4x^3 = 5.02 \times 10^{-6}\ x = 0.0108\text{ M}\ [\text{OH}^-] = 2x = 0.0216\text{ M}\ \text{pOH} = 1.666\ \text{pH} = 12.334$

Exercise $9.E.31$**

At the equivalence point enough acid has been added to neutralize all of the base:

$$\text{H}_3\text{O}^+\,(\text{aq}) + \text{CH}_3\text{NH}_2\,(\text{aq}) \rightarrow \text{CH}_3\text{NH}_3{}^+\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l})$$

moles CH_3NH_2 = moles HCl

$\text{mol}_{\text{CH}_3\text{NH}_2} = 0.100\ \frac{\text{mol}}{\text{L}}(0.0500\text{ L}) = 0.00500\text{ mol} = \text{mol}_{\text{HCl}}\ \frac{0.00500\text{ mol}}{0.125\ \frac{\text{mol}}{\text{L}}} = 0.0400\text{ L}$

To find the pH, we need the concentration of the conjugate acid, $\text{CH}_3\text{NH}_3{}^+$, present. For each mole of base that reacts, one mole of conjugate acid forms:

$$\text{H}_3\text{O}^+\,(\text{aq}) + \text{CH}_3\text{NH}_2\,(\text{aq}) \rightarrow \text{CH}_3\text{NH}_3{}^+\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l})$$

$[\text{CH}_3\text{NH}_3{}^+] = \frac{\text{mol}}{\text{total volume}} = \frac{0.00500\text{ mol}}{0.0900\text{ L}} = 0.0556\text{ M}$

	$\text{CH}_3\text{NH}_3{}^+\,(\text{aq})$ +	$\text{H}_2\text{O}\,(\text{l})$ ⇌	$\text{CH}_3\text{NH}_2\,(\text{aq})$ +	$\text{H}_3\text{O}^+\,(\text{aq})$
Initial	0.0556 M	X	0 M	0 M
Change	- x		+ x	+ x
Equilibrium	0.0556 - x		x	x

$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-11} = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3{}^+]} = \frac{x^2}{0.0556 - x}$

Since K_a is very small, the conjugate acid will only ionize slightly, and we can assume that x << 0.0556 M.

$K_a = \frac{x^2}{0.0556} = 2.2 \times 10^{-11}\ x = 1.1 \times 10^{-6}\text{ M}$

Checking assumption:

$\frac{1.1 \times 10^{-6}\ \text{M}}{0.0556\ \text{M}} \times 100\% = 0.0020\%$ (valid)

$\text{pH} = -\log\left[\text{H}_3\text{O}^+\right] = 5.96$

Exercise $9.E.32$**

$\text{CaCO}_3\,(\text{s}) \rightleftharpoons \text{Ca}^{2+}\,(\text{aq}) + {\text{CO}_3}^{2-}\,(\text{aq})$

In 0.10 M $\text{Na}_2\text{CO}_3\,(\text{aq})$, there are ${\text{CO}_3}^{2-}$ ions in the solution. The presence of this common ion will allow less CaCO_3 to dissolve.

In 0.10 M $\text{Ca}(\text{NO}_3)_2\,(\text{aq})$, there are Ca^{2+} ions in the solution. The presence of this common ions will allow less CaCO_3 to dissolve.

HCl can react with the ${\text{CO}_3}^{2-}$ ions formed from the dissolution of CaCO_3:

${\text{CO}_3}^{2-}\,(\text{aq}) + \text{H}_3\text{O}^+\,(\text{aq}) \rightarrow \text{HCO}_3^-\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l})$

This decreases the $[{\text{CO}_3}^{2-}]$ allowing more CaCO_3 to dissolve.

Conclusion: The solubility is highest in 0.10 M HCl due to the removal of ${\text{CO}_3}^{2-}$ by protonation, which shifts the equilibrium to the right.

Exercise $9.E.33$***

We can find the pK_a of the acid:

$$\text{pH} = pK_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

$$pK_a = \text{pH} - \log\frac{[\text{A}^-]}{[\text{HA}]} = 4.72 - \log\left(\frac{0.200\ \text{M}}{0.100\ \text{M}}\right) = 4.42$$

We know that HCl will ionize completely to produce \(\ce{H3O+}\), so we can write the neutralization reaction in terms of \(\ce{H3O+}\):

$$\text{A}^-\,(\text{aq}) + \text{H}_3\text{O}^+\,(\text{aq}) \rightarrow \text{HA}\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l})$$

The single reaction arrow indicates that this reaction goes to completion. First find the moles of all species:

$$\text{mol}_{\text{HA}} = (0.100\ \frac{\text{mol}}{\text{L}})(0.250\ \text{L}) = 0.0250\ \text{mol}$$

$$\text{mol}_{\text{A}^-} = (0.200\ \frac{\text{mol}}{\text{L}})(0.250\ \text{L}) = 0.0500\ \text{mol}$$

$$\text{mol}_{\text{HCl}} = \text{mol}_{\text{H}_3\text{O}^+} = (0.100\ \frac{\text{mol}}{\text{L}})(0.010\ \text{L}) = 0.00100\ \text{mol}$$

	$\text{A}^-\,(\text{aq}))\ +$	$\text{H}_3\text{O}^+\,(\text{aq})$ ⇳	$\text{HA}\,(\text{aq})\ +$	$\text{H}_2\text{O}\,(\text{l})$
Initial	0.0500 mol	0.00100 mol	0.0250 mol	X
Change	- 0.00100 mol	- 0.00100 mol	+ 0.00100 mol	
Final	0.0490 mol	0	0.0260 mol	

The total volume of the solution is 0.250 L (buffer solution) + 0.010 L (HCl) = 0.260 L

$$[\text{A}^-] = \frac{0.0490\ \text{mol}}{0.260\ \text{L}} = 0.188\ \text{M}$$

$$[\text{HA}] = \frac{0.0260\ \text{mol}}{0.260\ \text{L}} = 0.100\ \text{M}$$

$$\text{pH} = pK_a + \log\frac{[\text{A}^-]}{[\text{HA}]} = 4.42 + \log\left(\frac{0.188\ \text{M}}{0.100\ \text{M}}\right) = 4.69$$

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10: THERMODYNAMICS

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10.1: Introduction

Keeping Energy in Check: The Thermodynamics Behind Safer Batteries



Figure 10.1.1**:** A graphic with basic facts about Shirley Meng, materials chemist who has made amazing discove regarding solid-state batteries. Dr. Meng is a professor at the University of Chicago Pritzker School of Molecul Engineering and chief scientist at the Argonne Collaborative Center for Energy Storage Science (ACCESS) at t Argonne National Laboratory. Image from University of Chicago Pritzker School of Molecular Engineering; copyr 2025 University of Chicago.

Thermodynamics is the study of energy and its transformations. These principles help us understand whether a reaction will proceed and, if so, under what conditions. Although thermodynamics was originally developed to improve the efficiency of steam engines, its applications extend far beyond engines to include chemical reactions, biological processes, phase changes, refrigeration, and batteries.

Batteries are central to sustainable energy strategies, but current technologies are not yet capable of meeting global energy demands. Dr. Shirley Meng, a leading scientist in energy storage materials, is applying thermodynamic principles to help design next-generation solid-state, anode-free batteries. These batteries offer the promise of higher energy density, fewer safety risks, and faster charging compared to the traditional lithium-ion models used in today's electronics. Achieving that promise, however, requires mastering the thermodynamics of solid-solid interfaces, phase transitions, and ion mobility.

In conventional batteries, liquid electrolytes make good contact with the current collector (the part of the battery that conducts electrons to the external circuit), which helps the battery function efficiently. Over time, however, the liquid can break down and react with other materials in the battery. This creates unwanted buildup at the interface (where different battery components meet) which slowly consumes the active materials and reduces the battery's capacity. Solid-state batteries avoid this problem by using a solid electrolyte instead of a liquid one, but it is more difficult for the solid to maintain good contact with the current collector, creating a new challenge for battery design.

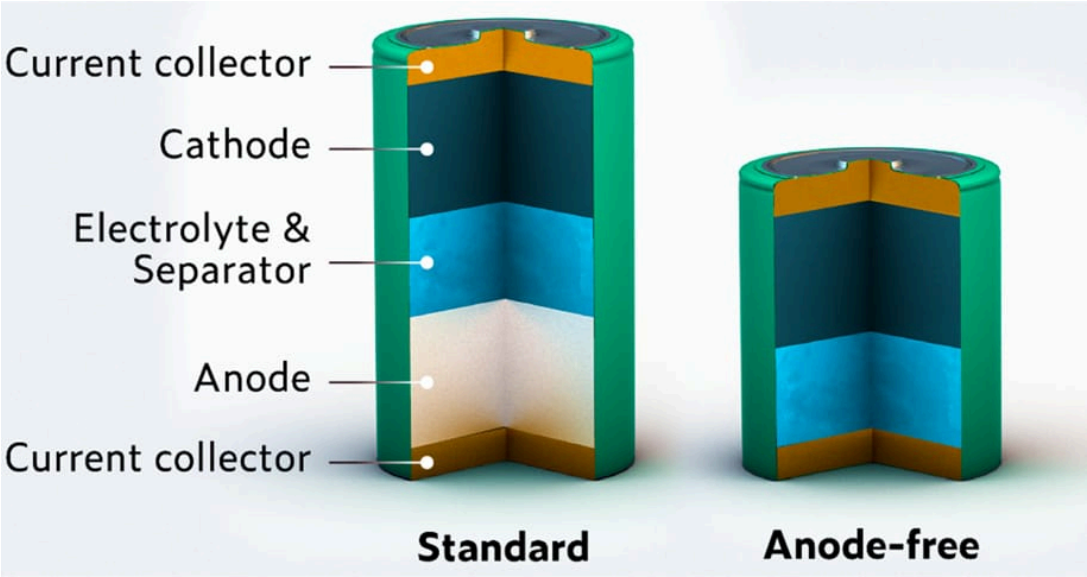


Figure 10.1.2**:** A schematic diagram of the difference between a standard battery and an anode-free battery. A standard battery consist cathode (a negatively charged electrode) and an anode (a positively charged electrode) separated by an electrolyte (a material contai ions), with a current collector (to connect to the external circuit) at each end. An anode-free battery has the same components except f anode, because the anode is actually formed during the first charge cycle. This reduces material costs and allows batteries to be ma smaller. Reprinted from with permission from Zhu et al. **2021**, Nano Letters *21*(3). Copyright 2025 American Chemical Society.

Dr. Meng and her research team use advanced computational tools to predict the structure of materials that are dense, make effective contact with the current collector, and are thermodynamically stable. In 2024, her group published design principles for these materials and demonstrated a sodium-containing solid-state battery material that can withstand over 400 charge cycles without significantly diminishing capacity. Her research shows how exploring new materials and characterizing their thermodynamic properties can improve battery lifespan, power, and safety, helping to prevent short circuits, fires and explosions.

By replacing scarce lithium with abundant sodium and improving performance through thermodynamic insight, Meng's work is paving the way for safer, more sustainable energy storage. Her research shows how thermodynamic properties like entropy and enthalpy, which describe the behaviour of materials at the atomic level, influence the performance and stability of real-world batteries. In this chapter, we will explore these same fundamental laws of thermodynamics.

Glossary

thermodynamics
: The study of energy and its transformations.

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10.2: Spontaneity

Learning Objectives

- Define spontaneous and nonspontaneous processes.
- Distinguish between spontaneity and rate of reaction.

Physical and chemical processes proceed in a particular direction under a given set of conditions. Water flows downhill without assistance, but moving it uphill requires a pump. Ice melts at room temperature, but liquid water does not spontaneously freeze under those same conditions. Iron rusts when exposed to air and moisture, but rust will not convert back to metallic iron without intervention.

These examples illustrate the concept of spontaneity. A spontaneous process is one that occurs on its own under a given set of conditions, without the need for continuous input of energy from the surroundings. Importantly, a spontaneous process may require an initial input of energy to begin, but once started, it proceeds without ongoing external energy. In contrast, a nonspontaneous process cannot occur under the given conditions unless it is continuously driven by energy from an external source.

If a process is spontaneous in one direction under certain conditions, the reverse process is nonspontaneous under those same conditions. For example, at room temperature and atmospheric pressure, ice melts spontaneously, but water does not spontaneously freeze.

It is important to distinguish between spontaneity and rate of reaction. A spontaneous process may be very fast or extremely slow. Spontaneity tells us whether a process can occur under certain conditions, not how quickly it will proceed.

For example, the conversion of diamond to graphite is thermodynamically spontaneous at room temperature and pressure (Figure 10.2.1):

$$\mathrm{C}(s,\ \text{diamond}\ ) \longrightarrow \mathrm{C}(s,\ \text{graphite}\ )$$

However, the process occurs so slowly that it is essentially unobservable on a human timescale. In contrast, combustion reactions are often both spontaneous and rapid. These examples highlight the distinction between thermodynamics, which addresses whether a process is energetically favorable, and kinetics, which describes how fast it happens.

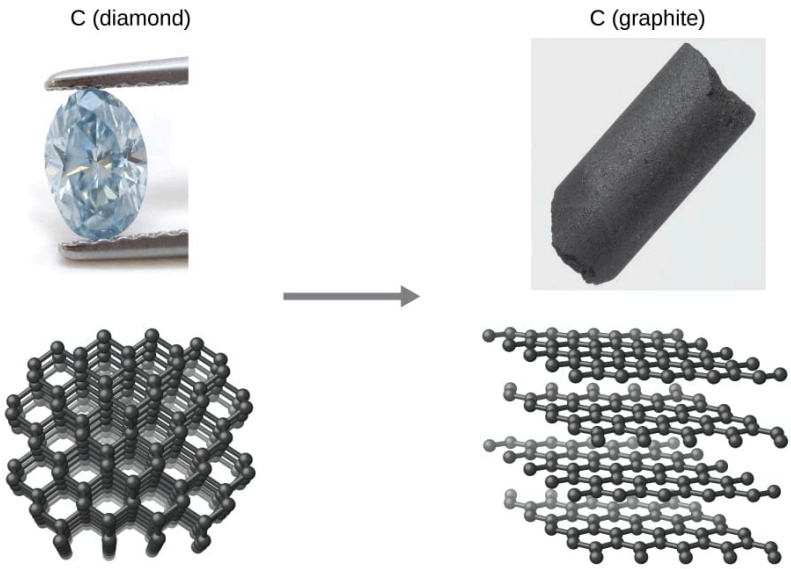


Figure 10.2.1: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

What determines if a process is spontaneous?

Many spontaneous chemical reactions release energy in the form of heat — they are exothermic. For instance, the combustion of fuels, the freezing of water, and the condensation of steam all occur spontaneously under appropriate conditions and give off heat. However, some exothermic processes are non-spontaneous and some endothermic processes may be spontaneous depending on the reaction conditions.

For example, ice melting at room temperature is spontaneous and endothermic. Instant cold packs become cold when activated, due to a spontaneous endothermic dissolution process (Figure 10.2.2).

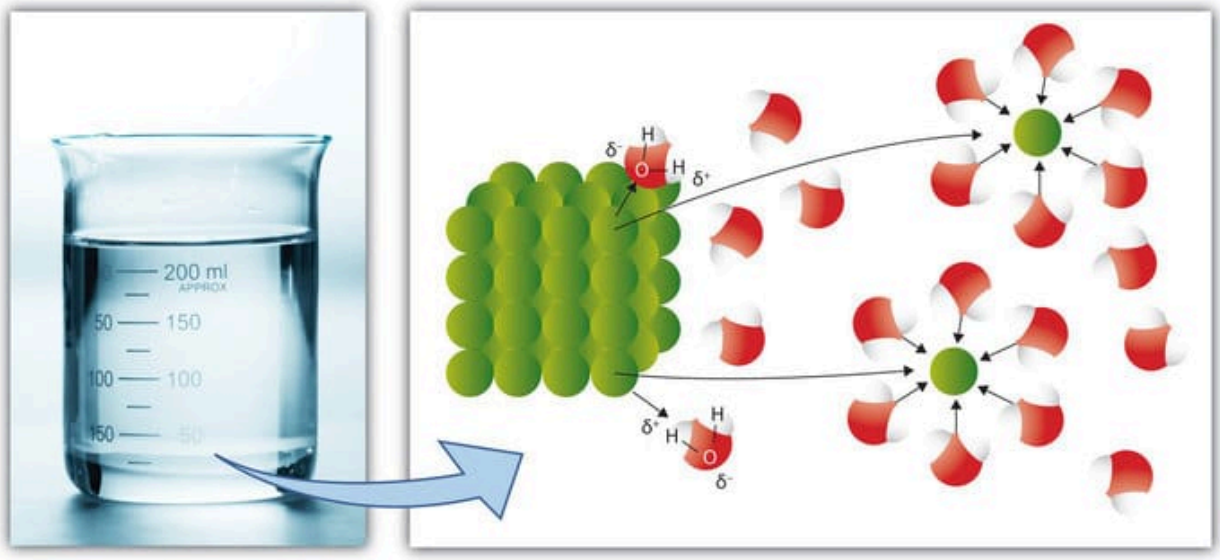


Figure 10.2.2: The molecular view of a solid dissolving in water. When a solute dissolves, the individual ions of the solid become surrounded by solvent particles and detach from the remaining solid. The ions are surrounded by solvent molecules in solution. Source: Photo © Thinkstock

These examples show that the release of energy is not the only factor that determines whether a process is spontaneous; they involve a deeper common feature related to particle behaviour.

What do the melting of ice and the dissolution process in an ice pack have in common?

In both cases, the resulting particles become more spread out and have greater freedom of motion than in the starting materials. For example, when ice melts, the molecules change from vibrating about fixed positions to moving and rotating freely in the liquid state.

In the next section, entropy, the measure of dispersion of energy in a system, will be described. We will see that both the change in enthalpy and the change in entropy of a process will affect the spontaneity.

Summary

Spontaneous processes proceed without continuous input of energy under given conditions, while nonspontaneous processes require ongoing external energy. If a process is spontaneous in one direction under certain conditions, the reverse process is nonspontaneous under those same conditions.

Spontaneity does not imply a fast rate of reaction. Although many spontaneous processes are exothermic, energy release alone does not determine spontaneity.

Glossary

nonspontaneous process
: A process that requires continual input of energy from an external source.

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

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10.3: Entropy

Learning Objectives

- Predict the sign of the entropy changes in simple chemical reactions or processes.
- Describe entropy in relation to the dispersal of energy in a system and connect this to the number of microstates.

In thermochemistry (Chapter 5), we saw that energy is conserved according to the First Law of Thermodynamics. Changes in the internal energy (ΔE) and the enthalpy (ΔH) of a system describe the flow of energy between a system and its surroundings. However, these quantities alone do not determine whether a process is spontaneous.

For example, if a hot frying pan is placed in a sink of cold water, heat flows from the frying pan to the water until they reach the same temperature. This heat flow obeys the First Law of Thermodynamics: energy is conserved. The reverse process, the frying pan becoming hotter while the water cools further, never happens spontaneously, even though energy would still be conserved.

These examples show that we need a new thermodynamic quantity, entropy, to understand why processes are spontaneous.

Entropy (S) is a thermodynamic quantity that measures the dispersal of energy in a system. Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the dispersal of energy in the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

The units of ΔS are J/(mol·K).

One way to calculate ΔS for a reaction is to use tabulated values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard pressure of 1 atm and often reported at 298 K. Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K (corresponding to S = 0 J/(mol·K) for perfect crystalline substances) and the desired final temperature, typically 298 K.

Trends in Entropy

Consider the phase changes illustrated in Figure $10.3.1$. In the solid phase, atoms or molecules are restricted to vibrating in nearly fixed positions. In the liquid phase, they are free to move over and around each other, though they remain in relatively close proximity. In the gas phase, the particles are much more widely dispersed and have much greater freedom of motion. Entropy increases because the number of possible arrangements of the particles and their motions increases with each phase change. For any substance: \[S_{\text{solid}}

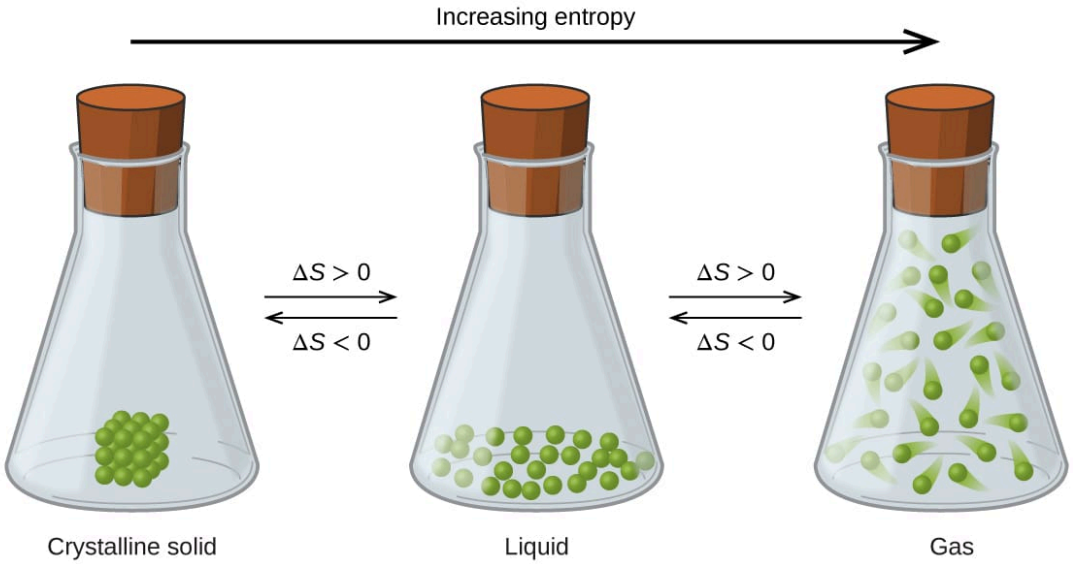


Figure 10.3.1: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. Entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

The temperature of a substance is proportional to the average kinetic energy of its particles. As temperature increases (Figure 10.3.2), molecules move more rapidly and can access a wider range of motions, including vibrations, rotations, and translations (Figure 10.3.3). These motions become more extensive at higher temperatures, resulting in a greater dispersal of energy and an increase in entropy. Thus, the entropy for any substance increases with temperature.

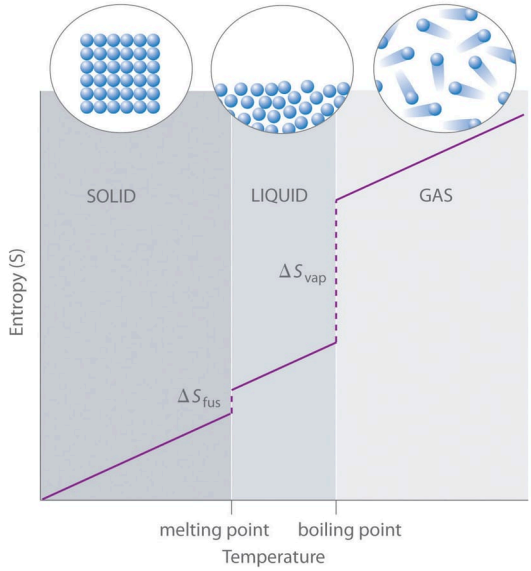


Figure 10.3.2: Entropy versus Temperature. Entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).

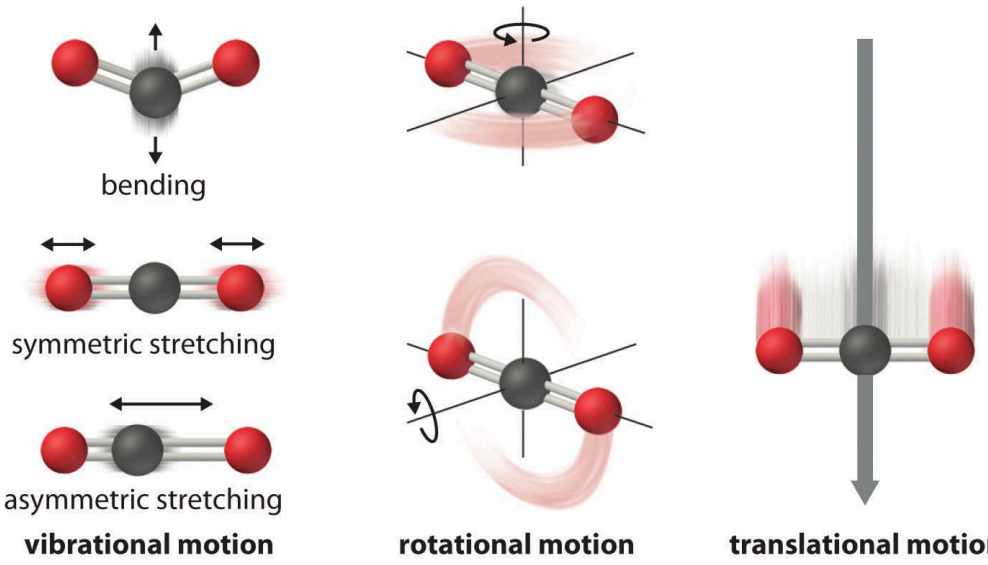


Figure 10.3.3: Molecular motions of a carbon dioxide molecule. Vibrational motion (left): the atoms within a molecule move relative to each other; Rotational motion (middle): the entire molecule rotates around any axis; Translational motion (right): the entire molecule moves in three dimensional space. These motions become more extensive at higher temperatures.

In addition, for substances in the same phase, entropy increases with molecular complexity, that is, with the number of atoms making up a molecule. The more atoms in the structure, the more molecular motions are possible. For example, carbon monoxide, (CO) has only one vibrational motion possible with the carbon and oxygen atoms moving together and apart, compared to the three vibrational motions of carbon dioxide (CO_2) shown in Figure 10.3.3. Correspondingly, the standard molar entropy of CO_2 is higher:

$$S^\circ(CO_2) = 213.8\ \text{J/(mol·K)}\ \text{vs}\ S^\circ(CO) = 197.7\ \text{J/(mol·K)}$$

Finally, variations in particle types affect the entropy of a system. Compared to a pure substance, a mixture of different types of particles has a greater entropy. This is due to the additional orientations and interactions possible among nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience greater freedom of motion and additional interactions with solvent particles. Dissolution typically results in an increase in entropy ($\Delta S > 0$).

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes, as illustrated in Example 10.3.1.

Example 10.3.1: Predicting the Sign of ΔS

Predict the sign of the entropy change (ΔS) for the following processes. Explain your prediction.

a. Heating one mole of liquid water from room temperature to 50 °C
b. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
c. $C_6H_6(l) + \frac{15}{2}\ O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$
d. $NH_3(s) \longrightarrow NH_3(l)$

Solution

a. Entropy increases ($\Delta S > 0$); temperature increases, leading to greater molecular motion.
b. Entropy decreases ($\Delta S < 0$); ions combine to form a solid, reducing dispersal of matter.
c. Entropy decreases ($\Delta S < 0$); net decrease in the number of gaseous molecules.
d. Entropy increases ($\Delta S > 0$); phase change from solid to liquid increases freedom of motion.

Exercise 10.3.1

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3\,(s)\ \rightarrow Na^+\,(aq) + NO_3{}^-\,(aq)}$
b. Freezing of liquid water
c. $\mathrm{CO_2\,(s)\ \rightarrow CO_2\,(g)}$
d. $\mathrm{CaCO_3\,(s)\ \rightarrow CaO\,(s) + CO_2\,(g)}$

Answer available at the end of this section.

Microstates

Entropy corresponds to a larger dispersal of energy and more probable states. To understand why, we can examine entropy at the molecular scale. High-entropy states, which have greater energy dispersal and greater freedom of motion, can be achieved in more ways than low-entropy states. As a result, high-entropy states are more probable.

The entropy of a system can be related to the number of microstates (W) available to it. A microstate is a specific arrangement of all the positions and energies of the atoms or molecules that make up a system at a specific total energy. The relationship between a system's entropy and the number of possible microstates is given by the Boltzmann equation:

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38 x 10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final and initial values:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}}$$

If the number of microstates increases during a process ($W_{\text{final}} > W_{\text{initial}}$), the entropy of the system increases and $\Delta S > 0$. If the number of microstates decreases during a process (\W_{\text{final}}

Suppose four gas molecules are initially confined to one side of a two-bulb container (Figure $10.3.4$). In this case, there is only one possible microstate: all four molecules must be in the same bulb.

When the valve between the bulbs is opened, the molecules are free to occupy either bulb. If we (artificially) distinguish the molecules by colour, we can see that there are 16 possible microstates overall. Some macroscopic arrangements (like all molecules in one bulb) correspond to just one microstate. Other arrangements (like two molecules in each bulb) correspond to multiple microstates.

- Arrangement I: 1 microstate
- Arrangement II: 4 microstates
- Arrangement III: 6 microstates
- Arrangement IV: 4 microstates
- Arrangement V: 1 microstate

Because the number of microstates increases when the molecules have more available space, the entropy of the system also increases.
Expansion increases entropy by increasing the number of accessible microstates.

Quantitatively, initially, there was one available microstate, $W_{\text{initial}} = 1$. Thus:

$$S_{\text{initial}} = k \ln(1) = (1.38 \times 10^{-23}\ \text{J/K})(0) = 0$$

Here, $S_{\text{initial}} = 0$ means that in this simplified model, there is only one possible arrangement of molecules. It does not mean the gas actually has zero entropy; in reality, molecules have many other microstates from translational, rotational, vibrational, and

electronic motion.

After the valve is opened, each of the four molecules ($N = 4$) can be in either bulb (2 possible locations), leading to 16 microstates:

$$W_{\text{final}} = 2^N = 2^4 = 16$$

$$S_{\text{final}} = k \ln W = (1.38 \times 10^{-23}\ \text{J/K}) \ln(16) = 3.83 \times 10^{-23}\ \text{J/K}$$

This calculation confirms the conceptual idea: when the available volume increases, the number of positional microstates increases, and so does the entropy.

Note: This example focuses on the changes in microstates relating to the changes in the positions of the molecules in the two bulbs. Real gases have many more microstates, even before expansion, so their entropy is always greater than zero.

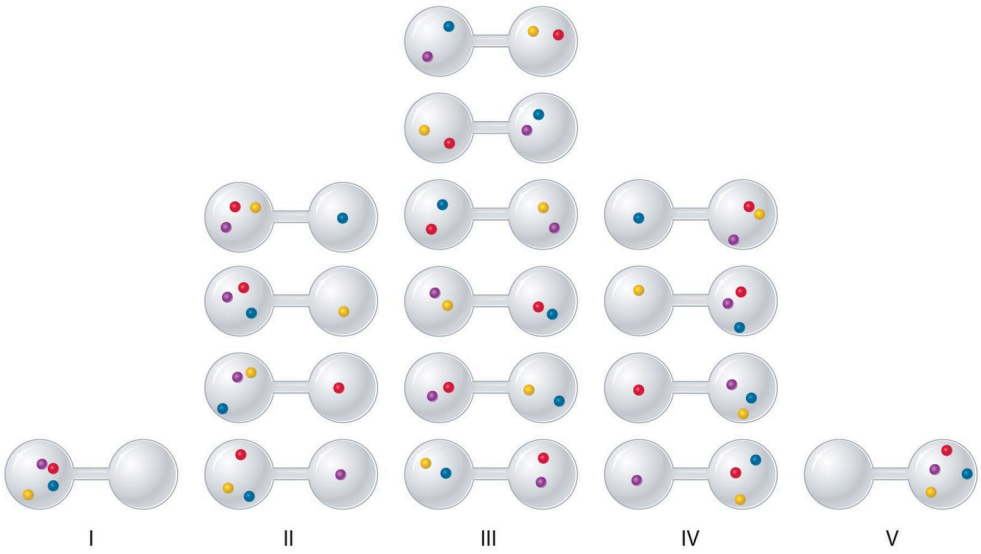


Figure 10.3.4: Distribution of four gas molecules between two connected containers.

Now imagine a real gas sample with 2.69 × 10^{22} molecules in a 1.00 L container. If this gas is allowed to expand into a second connected 1.00 L container, the number of positions available to each molecule doubles. The number of possible microstates is proportional to the volume and number of particles that make up the system:

$$W \propto V^N$$

Increasing the volume by a factor of 2 results in an increase of the number of possible microstates by 2. The change in entropy upon changing the volume is:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}} = k \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right)^N$$

$$= 1.38 \times 10^{-23}\ \text{J/K} \ln \left(\frac{2.00\ \text{L}}{1.00\ \text{L}} \right)^{2.69 \times 10^{22}} = 1.38 \times 10^{-23}\ \text{J/K} (2.69 \times 10^{22}) \ln 2 = 0.257\ \text{J/K}$$

This simple calculation shows that increasing the number of available microstates leads to an increase in entropy.

Although we will not use Boltzmann's equation for entropy calculations in CHM 135H, reviewing these calculations helps develop a conceptual understanding of the relationship between microstates, probability, and entropy.

Let's look back at phase changes in terms of microstates:

- Solid to liquid (melting):
  In a solid, atoms or molecules occupy fixed positions in a lattice. In a liquid, particles are free to move and tumble, allowing many more microstates.
  $\Delta S_{\text{fus}} > 0$

- Liquid to gas (vaporization):
  Molecules in a gas have even greater freedom of motion than in a liquid, so
  $\Delta S_{\text{vap}} > 0$

Conversely, the reverse processes, condensation and freezing, reduce freedom of motion and the number of microstates, and thus decrease entropy.

Each increase in freedom of motion corresponds to an increase in the number of accessible microstates, making higher-entropy states both more probable and more stable.

Example 10.3.2: Comparing Entropies based on Microstates

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $\mathrm{NH_3\,(g)}$ or 1 mol of $\mathrm{He\,(g)}$, both at 25°C
b. 1 mol of $\mathrm{Pb\,(s)}$ at 25°C or 1 mol of $\mathrm{Pb\,(l)}$ at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of $\mathrm{NH_3}$ molecules. With four atoms instead of one, the $\mathrm{NH_3}$ molecules have more motions available, leading to a greater number of microstates. Hence we predict that the $\mathrm{NH_3}$ sample will have the higher entropy.
b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid (more microstates), we predict that the liquid sample will have the higher entropy.

Summary

Entropy (S) is a state function that measures the dispersal of energy in a system and is related to the number of accessible microstates. A greater number of microstates corresponds to a more probable state and a higher entropy.

Entropy increases with temperature, phase changes (solid → liquid → gas), molecular complexity, and mixing.

Glossary

entropy (S)
A state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system.

entropy change (ΔS)
The increase or a decrease in the dispersal of energy in the system during a chemical or physical change.

microstate (*W*)
A possible configuration or arrangement of matter and energy within a system.

standard molar entropy (S°)
The entropy of 1 mol of substance at a standard pressure of 1 atm.

Answers

Exercise 10.3.1

a. Positive; the solid dissolves, increasing the number of mobile ions.
b. Negative; the liquid becomes a more ordered solid.
c. Positive; the ordered solid becomes a gas.
d. Positive; a gas forms

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10.4: The Second and Third Laws of Thermodynamics

Learning Objectives

- State and explain the Second and Third Laws of Thermodynamics
- Calculate standard entropy changes (ΔS°) for chemical reactions using tabulated standard molar entropy values.

The First Law of Thermodynamics tells us that energy is conserved in all processes, but it does not tell us whether a process will occur spontaneously. We have seen that entropy is related to spontaneity, but the change in entropy of the system alone is not enough to determine whether a process is spontaneous. For example, ice melting has a positive entropy change for the system and is spontaneous at room temperature, while ice freezing has a negative entropy change for the system and is spontaneous at –10 °C. The spontaneity of each depends not only on the system, but also on the surroundings. The Second Law of Thermodynamics links entropy to spontaneity by considering both the system and surroundings.

The Second Law of Thermodynamics

The second law of thermodynamics states that processes occur spontaneously in the direction that increases the entropy of the universe.

That is:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

- $\Delta S_{\text{univ}} > 0$: spontaneous
- $\Delta S_{\text{univ}} < 0$: nonspontaneous (spontaneous in opposite direction)
- $\Delta S_{\text{univ}} = 0$: at equilibrium (both directions are spontaneous)

This means that a spontaneous process can involve a decrease in entropy for either the system or the surroundings, as long as the total entropy of the universe increases.

In chemistry, we usually focus on the system (a chemical reaction or phase change), but entropy is a property of both the system and the surroundings.

For example, when ice melts at room temperature, the system absorbs heat and the entropy of the water increases as molecules gain more freedom of motion. Heat is lost by the surroundings, so the entropy of the surroundings decreases slightly. However, the increase in entropy of the system is greater than the decrease in the surroundings, so the total entropy increases. The process is spontaneous.

Now consider a spontaneous chemical reaction in which entropy of the system decreases, the combustion of methane:

$$\mathrm{CH_4\,(g) + 2\,O_2\,(g)} \rightarrow \mathrm{CO_2\,(g) + 2\,H_2O\,(l)} \quad \Delta H^\circ = -890\ \mathrm{kJ/mol}$$

In this reaction, there are fewer moles of gases in the products compared to the reactants, so ΔS_{sys} is negative. Since the reaction is spontaneous, the total entropy must still increase. How? The reaction is exothermic, releasing heat to the surroundings. That heat increases the entropy of the surroundings enough to outweigh the decrease in the system.

More generally,

- Exothermic reactions ($q_{\text{sys}} < 0$) heat the surroundings ($q_{\text{surr}} > 0$), which increases the entropy of the surroundings ($\Delta S_{\text{surr}} > 0$).
- Endothermic reactions ($q_{\text{sys}} > 0$) absorb heat from the surroundings ($q_{\text{surr}} < 0$), which decreases the entropy of the surroundings ($\Delta S_{\text{surr}} < 0$).

The temperature also matters. Releasing heat into cold surroundings increases entropy more than releasing the same amount into warmer surroundings:

$$\Delta S_{\text{surr}} \propto \frac{q_{\text{surr}}}{T}$$

(More details about this relationship will be introduced in more advanced courses)

In practice, it's difficult to calculate entropy changes for the surroundings directly, especially when heat flow isn't easily measured. Fortunately, at constant temperature and pressure, we can use a new quantity called Gibbs free energy to determine spontaneity by looking only at the system. That is the focus of the next section.

The Third Law of Thermodynamics

The Third Law of Thermodynamics provides an absolute reference point for measuring entropy. It states that the entropy of a perfect crystalline substance, where all the particles are in a regular uniform array, is zero at absolute zero (0 K).

At 0 K, all atomic and molecular motion stops, and there is only one possible arrangement (microstate) for the particles of a perfect crystalline substance. Since entropy is a measure of the number of accessible microstates, the entropy is defined as exactly zero at that point: S = 0 J/(mol · K) at T = 0 K.

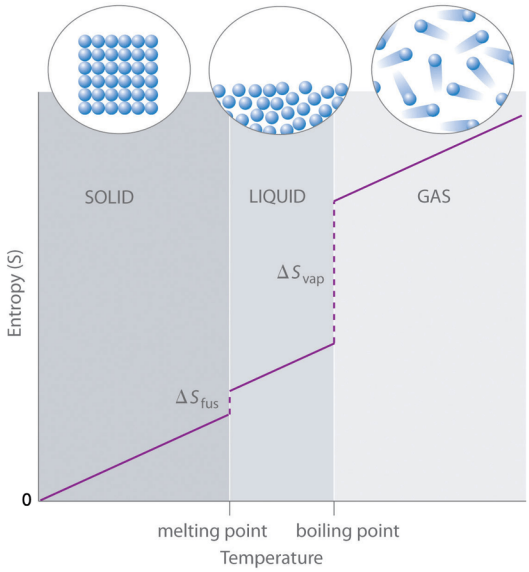


Figure 10.4.1: Entropy versus Temperature. At 0 K, the entropy of a perfect crystalline substance is 0 J/(mol · K).

Because of this, it is possible to determine absolute entropy values for substances by measuring the entropy change from 0 K up to a desired final temperature (usually 298 K). This is different from enthalpy, where we define the enthalpy of formation of elements in their standard state as zero. As a result, standard molar entropies (S°) are never zero, even for pure elements in their most stable forms. This absolute scale allows us to compare entropy values directly and calculate entropy changes for reactions. Standard entropy changes for chemical reactions can be calculated using tabulated values and the following expression:

$$\Delta S^\circ = \sum mS^\circ_{\text{products}} - \sum nS^\circ_{\text{reactants}}$$

As with standard enthalpies of formation, m and n represent the stoichiometric coefficient of each product and reactant, respectively. These values allow us to calculate entropy changes and will be useful when predicting spontaneity in the next section.

Some substances are not perfectly crystalline at 0 K. This happens when the molecules that make up the crystal are able to adopt multiple almost equally favourable orientations. In this case, $W > 1$ and $\Delta S > 0$ at T = 0 K. The entropy at T = 0 K of non-perfect crystalline substances is called the residual entropy. Although not equal to zero, residual entropies are still very small in value due to the absence of thermal molecular motion, and are often ignored when calculating standard molar entropies (S°).

Example 10.4.1: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, $\mathrm{CH_3OH}$:

$$2\,\mathrm{CH_3OH\,(l)} + 3\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} + 4\,\mathrm{H_2O\,(l)}$$

The values for the standard molar entropies can be found in the reference table.

Explain the sign of the entropy change in terms of particle motion and the number of possible microstates.

Solution

Calculate the entropy change using standard entropies as shown above:

$$\begin{aligned}\Delta S^\circ &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \\ &= [2 \times S^\circ(\mathrm{CO_2\,(g)}) + 4 \times S^\circ(\mathrm{H_2O\,(l)})] - [2 \times S^\circ(\mathrm{CH_3OH\,(l)}) + 3 \times S^\circ(\mathrm{O_2\,(g)})] \\ &= [2(213.8\ \mathrm{J/(mol \cdot K)}) + 4(70.0\ \mathrm{J/(mol \cdot K)})] - [2(126.8\ \mathrm{J/(mol \cdot K)}) + 3(205.2\ \mathrm{J/(mol \cdot K)})] \\ &= -161.6\ \mathrm{J/(mol \cdot K)}\end{aligned}$$

The standard entropy change for this reaction is negative because the moles of gas decrease as the reaction occurs, leading to less dispersion of energy, a reduction in the number of adopted microstates, and thus lower entropy.

Exercise 10.4.1

Calculate the standard entropy change for the following reaction:

$$\mathrm{Ca(OH)_2\,(s)} \longrightarrow \mathrm{CaO\,(s)} + \mathrm{H_2O\,(l)}$$

The values for the standard molar entropies can be found in the reference table.

Explain the sign of the entropy change in terms of particle motion and the number of possible microstates.

Answer available at the end of this section.

Summary

The Second Law of Thermodynamics states that spontaneous processes increase the total entropy of the universe.

The Third Law of Thermodynamics states that a perfect crystal has zero entropy at absolute zero (0 K). This establishes an absolute scale for entropy, making it possible to calculate entropy changes using standard molar entropies.

The standard entropy of a reaction, ΔS°, can be calculated from the standard entropies of the reactants and products.

Glossary

second law of thermodynamics
: The entropy of the universe increases for a spontaneous process.

standard entropy change (ΔS°)
: The change in entropy for a reaction calculated using the standard entropies, usually at room temperature.

third law of thermodynamics
: The entropy of a perfect crystal at absolute zero (0 K) is zero.

Answers

Exercise 10.4.1

$$\begin{aligned}\Delta S^\circ &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \\ &= [1 \times S^\circ(\text{CaO}\,(\text{s})) + 1 \times S^\circ(\text{H}_2\text{O}\,(\text{l}))] - [1 \times S^\circ(\text{Ca(OH)}_2\,(\text{s}))] \\ &= [38.1\ \text{J/(mol}\cdot\text{K)} + 70.0\ \text{J/(mol}\cdot\text{K)}] - [83.4\ \text{J/(mol}\cdot\text{K)}] \\ &= 24.7\ \text{J/(mol}\cdot\text{K)}\end{aligned}$$

This aligns with our expectation: forming a liquid from a solid increases the motion and number of arrangements a molecule can adopt, and thus the number of microstates of the system, resulting in a positive entropy change.

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10.5: Free Energy

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate the free energy change of a process using standard free energies of formation
- Calculate the free energy change of a process using enthalpy and entropy values
- Explain how temperature affects the spontaneity of some processes

The Second Law of Thermodynamics states that a spontaneous process increases the total entropy of the universe. This involves calculating the entropy change for both the system and the surroundings. To reduce calculations to just the system, Josiah Willard Gibbs introduced a new thermodynamic quantity: the Gibbs free energy, G. This quantity depends only on system properties, enthalpy, entropy, and temperature, and allows us to predict spontaneity of a process at constant temperature and pressure without considering the surroundings.

The Gibbs free energy (G) is defined as:

$$G = H - TS$$

At constant temperature and pressure, the free energy change (ΔG) is:

$$\Delta G = \Delta H - T\Delta S \tag{10.5.1}$$

This equation gives us a simple way to predict spontaneity at constant temperature and pressure, as shown in Table $10.5.1$:

Table $10.5.1$*: Relation between Process Spontaneity and Signs of Thermodynamic Properties*

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	Spontaneous in the forward direction; Nonspontaneous in the reverse direction
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	Nonspontaneous in the forward direction; Spontaneous in the reverse direction
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	At equilibrium; Both directions are spontaneous

As seen in Table $10.5.1$, while a positive value of ΔS_{univ} indicates a spontaneous process, a negative value of ΔG is an indicator of spontaneity. This stems from the relationship between ΔG and ΔS_{univ}, defined at constant temperature and pressure as:

$$\Delta G = \Delta G_{\text{sys}} = -T\Delta S_{\text{univ}}$$

What's "Free" about ΔG?

In addition to predicting spontaneity at constant temperature and pressure, the free energy change (ΔG) tells us about the amount of useful work a process can do.

Let's revisit the definition:

$$\Delta G = \Delta H - T\Delta S$$

In this equation:

- ΔH is the total heat released or absorbed by the system.
- $T\Delta S$ represents the energy of the system that is lost to disorder and is no longer available to do work.
- The remaining energy, ΔG , is “free” in the sense that it is the amount of energy left that can be harnessed to do useful work.

If a process is spontaneous and could occur reversibly (idealized conditions), then:

$$\Delta G = w_{\max}$$

That is, the free energy change equals the maximum amount of non-expansion work that can be obtained from a system under reversible conditions.

In real systems, however, no process is perfectly reversible, and devices like batteries or engines are never 100% efficient. So the actual work done is always less than ΔG.

Similarly, for a nonspontaneous process, $\Delta G > 0$ represents the minimum amount of work that must be done on the system to make the process happen.

Calculating Free Energy Change

Free energy (G) combines three state functions, enthalpy (H), entropy (S), and temperature (T), so it is also a state function. As with enthalpy, we focus on the free energy changes (ΔG). As we saw with other thermodynamic parameters, we can define the standard free energy change (ΔG°) as the free energy change that occurs when all components of the system are at standard state: 1 atm total pressure and 1 M concentration for solutions. We can write the following relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We have seen that standard enthalpy and entropy changes can be calculated from tabulated values. These allow us to determine ΔG° for a reaction under standard conditions.

The sign of ΔG° tells us which direction a reaction will proceed under standard conditions, and therefore whether the products or reactants are favoured.

If $\Delta G^\circ < 0$, the reaction is spontaneous and products are favoured.

If $\Delta G^\circ > 0$, the reaction is nonspontaneous and reactants are favoured.

If $\Delta G^\circ = 0$, the system is at equilibrium under standard conditions.

Example 10.5.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is -187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- $S^\circ(\mathrm{H_2O_2})$ = 109.6 J/(mol · K),
- $S^\circ(\mathrm{O_2})$ = 205.2 J/(mol · K), and
- $S^\circ(\mathrm{H_2})$ = 130.7 J/(mol · K).

Is the reaction spontaneous as written under standard state conditions and at 25°C?

Given: balanced chemical equation, ΔH° and ΔS° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. To calculate ΔG° for the reaction, we need to know ΔH°, ΔS°, and T. We are given ΔH°, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided.
B. Use Equation 10.5.1, the calculated value of ΔS°, and the given ΔH° and temperature to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous under standard state conditions.

Solution

A. Calculate ΔS° from the absolute molar entropy values provided using the formula: sum of entropies of products minus sum of entropies of reactants:

$$\begin{aligned}\Delta S^\circ &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})\\ \Delta S^\circ &= S^\circ(\mathrm{H_2O_2\,(l)}) - [S^\circ(\mathrm{H_2\,(g)}) + S^\circ(\mathrm{O_2\,(g)})]\\ &= 109.6\ \mathrm{J/(mol\cdot K)} - [130.7\ \mathrm{J/(mol\cdot K)} + 205.2\ \mathrm{J/(mol\cdot K)}]\\ &= -226.3\ \mathrm{J/(mol\cdot K)}\end{aligned}$$

Given the reaction consumes gas to form a liquid, ΔS° is very negative for this reaction as expected.

B. Substituting the appropriate quantities into Equation 10.5.1,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})\left(-226.3\ \frac{\mathrm{J}}{\mathrm{mol\cdot K}}\right)\left(\frac{\mathrm{kJ}}{1000\ \mathrm{J}}\right)\\ &= -120.31\ \mathrm{kJ/mol}\end{aligned}$$

The negative value of ΔG° indicates that the reaction is spontaneous in the forward direction under standard state conditions (1 atm $\mathrm{H_2\,(g)}$, 1 atm $\mathrm{O_2\,(g)}$ and 1 M $\mathrm{H_2O_2\,(l)}$ present).

Because both ΔS° and ΔH° are negative, the sign of ΔG° depends on the relative magnitudes of the ΔH° and $T\Delta S^\circ$ terms. At 298 K, the enthalpy term dominates, so the forward reaction is spontaneous.

Exercise 10.5.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$2\,\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)} \rightleftharpoons \mathrm{N_2H_4\,(l)}$$

Is this reaction spontaneous under standard state conditions (1 atm, 1 M) and at 25°C?

At 25°C, the standard enthalpy change (ΔH°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- $S^\circ(\mathrm{N_2H_4})$ = 121.2 J/(mol · K),
- $S^\circ(\mathrm{N_2})$ = 191.6 J/(mol · K), and
- $S^\circ(\mathrm{H_2})$ = 130.7 J/(mol · K).

Answer available at the end of this section.

We can also calculate the standard free energy change (ΔG°) for a reaction using standard free energies of formation ΔG_f° of the reactants and products. The standard free energy of formation is the free energy change of the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpy of formation, ΔG_f° is by definition zero for elemental substances in their standard states. The approach used to calculate ΔG° for a reaction from ΔG_f° values is the same as that demonstrated previously for enthalpy:

$$\Delta G^\circ = \sum mG_f^\circ(\text{products}) - \sum nG_f^\circ(\text{reactants})$$

Example 10.5.2: Using Standard Free Energies of Formation to Calculate $\Delta G°$

Consider the decomposition of yellow mercury(II) oxide.

$$\text{HgO}\,(\text{s, yellow}) \rightleftharpoons \text{Hg}\,(\text{l}) + \tfrac{1}{2}\,\text{O}_2\,(\text{g})$$

Calculate the standard free energy change at room temperature at 25°C, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies.

Is this reaction spontaneous under standard state conditions (1 atm, 1 M) and at 25°C?

The required data are shown here.

Compound	$\Delta G_f^\circ(\text{kJ/mol})$	$\Delta H_f^\circ(\text{kJ/mol})$	$S^\circ(\text{J/(mol·K)})$
HgO (s, yellow)	−58.43	−90.46	71.13
$\text{Hg}\,(\text{l})$	0	0	75.9
$\text{O}_2\,(\text{g})$	0	0	205.2

Solution

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ &= \sum mG_f^\circ(\text{ products }) - \sum n\Delta G_f^\circ(\text{ reactants }) \\ &= \left[1\Delta G_f^\circ\,(\text{Hg}\,(\text{l})) + \frac{1}{2}\Delta G_f^\circ\,(\text{O}_2\,(\text{g}))\right] - 1\Delta G_f^\circ\,(\text{HgO}\,(\text{s, yellow})) \\ &= \left[1(0\text{ kJ/mol}) + \frac{1}{2}(0\text{ kJ/mol})\right] - 1(-58.43\text{ kJ / mol}) = 58.43\text{ kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ &= \sum m\Delta H_f^\circ(\text{ products }) - \sum n\Delta H_f^\circ(\text{ reactants }) \\ &= \left[1\Delta H_f^\circ\,(\text{Hg}\,(\text{l})) + \frac{1}{2}\Delta H_f^\circ\,(\text{O}_2\,(\text{g}))\right] - 1\Delta H_f^\circ\,(\text{HgO}\,(\text{s, yellow})) \\ &= \left[1(0\text{ kJ/mol}) + \frac{1}{2}(0\text{ kJ/mol})\right] - 1(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol} \\ \Delta S^\circ &= \sum m\Delta S^\circ(\text{ products }) - \sum n\Delta S^\circ(\text{ reactants }) \\ &= \left[1\ \Delta S^\circ\,(\text{Hg}\,(\text{l})) + \frac{1}{2}\Delta S^\circ\,(\text{O}_2\,(\text{g}))\right] - 1\Delta S^\circ\,(\text{HgO}\,(\text{s, yellow})) \\ &= \left[1(75.9\text{ J /(mol·K)}) + \frac{1}{2}(205.2\text{ J/(mol·K)})\right] - 1(71.13\text{ J/(mol·K)}) = 107.4\text{ J/(mol·K)}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 90.46\text{ kJ/mol} - (298.15\text{ K})(107.4\text{ J/(mol·K)})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right) \\ &= 58.45\text{ kJ/mol}\end{aligned}$$

Both methods give the same ΔG° value at 25 °C (to three significant figures), confirming the reliability of either approach. The positive value means that the reaction is nonspontaneous under standard state conditions.

Exercise 10.5.2

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (values in the reference table). Is the reaction spontaneous or nonspontaneous at 25 °C under standard state conditions?

$$\mathrm{C_2H_4\,(g)} \rightleftharpoons \mathrm{H_2\,(g)} + \mathrm{C_2H_2\,(g)}$$

Answer available at the end of this section.

ΔG° predicts spontaneity at constant temperature and pressure and under standard conditions (1 M and 1 atm). Non-standard conditions (e.g., different concentrations or pressures) will be addressed later in the chapter.

Free Energy Changes for Coupled Reactions

In multi-step reactions, a nonspontaneous step can be driven by a spontaneous step if the overall free energy change is negative. This is how many biological and industrial reactions proceed. In these coupled reactions, one step supplies sufficient free energy for the other step to occur. Because free energy is a state function, we can combine ΔG values just as we combined enthalpy changes using Hess's Law (Ch. 5).

For example, the production of elemental zinc from zinc sulfide is nonspontaneous under standard conditions, as indicated by a positive value for ΔG°:

$$\mathrm{ZnS\,(s)} \rightleftharpoons \mathrm{Zn\,(s)} + \mathrm{S\,(s)} \quad \Delta G_1^\circ = 201.3\ \mathrm{kJ/mol}$$

The industrial process involves coupling this decomposition reaction to the thermodynamically favourable oxidation of sulfur:

$$\mathrm{S\,(s)} + \mathrm{O_2\,(g)} \rightleftharpoons \mathrm{SO_2\,(g)} \quad \Delta G_2^\circ = -300.1\ \mathrm{kJ/mol}$$

The coupled reaction, the sum of the two equations, has a negative free energy change and is therefore spontaneous:

$$\mathrm{ZnS\,(s)} + \mathrm{O_2\,(g)} \rightleftharpoons \mathrm{Zn\,(s)} + \mathrm{SO_2\,(g)}$$

$$\Delta G^\circ = 201.3\ \mathrm{kJ/mol} + (-300.1\ \mathrm{kJ/mol}) = -98.8\ \mathrm{kJ/mol}$$

The overall negative value of ΔG° means that the coupled process, decomposing zinc sulfide while oxidizing sulfur, is spontaneous under standard state conditions.

Let's consider another possible coupling pathway and assess its spontaneity.

Example 10.5.3: Calculating Free Energy Change for a Coupled Reaction

An industrial chemist considers coupling the decomposition of ZnS to the formation of $\mathrm{H_2S}$:

$$\mathrm{ZnS\,(s)} \rightleftharpoons \mathrm{Zn\,(s)} + \mathrm{S\,(s)} \quad \Delta G_1^\circ = 201.3\ \mathrm{kJ/mol}$$

$$\mathrm{H_2\,(g)} + \mathrm{S\,(s)} \rightleftharpoons \mathrm{H_2S\,(g)} \quad \Delta G_2^\circ = -33.4\ \mathrm{kJ/mol}$$

Is the coupled reaction spontaneous under standard conditions?

Solution

Decomposition of zinc sulfide:	$\mathrm{ZnS\,(s)} \rightleftharpoons \mathrm{Zn\,(s)} + \mathrm{S\,(s)}$	$\Delta G_1^\circ = 201.3\ \mathrm{kJ/mol}$
Formation of hydrogen sulfide:	$\mathrm{S\,(s)} + \mathrm{H_2\,(g)} \rightleftharpoons \mathrm{H_2S\,(g)}$	$\Delta G_2^\circ = -33.4\ \mathrm{kJ/mol}$
Coupled reaction:	$\mathrm{ZnS\,(s)} + \mathrm{H_2\,(g)} \rightleftharpoons \mathrm{Zn\,(s)} + \mathrm{H_2S\,(g)}$	$\Delta G^\circ = 201.3\ \mathrm{kJ/mol} + (-33.4\ \mathrm{kJ/mol}) = 167.9\ \mathrm{kJ/mol}$

Because the total ΔG° is positive (+167.9 kJ/mol), the overall reaction is nonspontaneous under standard conditions and would require input of external energy to proceed.

Temperature Dependence of Spontaneity

As we saw earlier in this chapter, the spontaneity of a process can depend on temperature. For example, phase transitions proceed spontaneously in one direction or the other depending on the temperature. Similarly, some chemical reactions are spontaneous in the forward direction at certain temperatures and spontaneous in the reverse direction at others.

To illustrate this, consider the expression for standard free energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

When ΔG° is negative, the forward reaction is spontaneous under standard state conditions, and products are favoured. When ΔG° is positive, the reverse reaction is spontaneous, and reactants are favoured. Since temperature (in Kelvin) is always positive, the sign of ΔG° depends on the signs and relative magnitudes of ΔH° and ΔS°. Depending on the signs of ΔH° and ΔS°, there are four possible combinations:

1. **Both ΔH° and ΔS° are positive:**
   - This describes an endothermic process with an increase in entropy. ΔG° will be negative if the magnitude of the $T\Delta S^\circ$ term is greater than ΔH°. At higher temperatures, ΔG° will be negative and the forward reaction spontaneous. At lower temperatures, the reverse will be true: ΔG° will be positive and the reverse reaction spontaneous.
2. **Both ΔH° and ΔS° are negative:**
   - This describes an exothermic process with a decrease in entropy. ΔG° will be negative if the magnitude of the $T\Delta S^\circ$ term is less than ΔH°. At lower temperatures, the forward reaction is spontaneous. At higher temperatures, the $T\Delta S^\circ$ term is greater than ΔH°, giving a positive ΔG°.
3. **ΔH° is positive and ΔS° is negative:**
   - This describes an endothermic process with a decrease in system entropy. ΔG° will be positive at all temperatures. The reaction is never spontaneous in the forward direction under standard conditions.
4. **ΔH° is negative and ΔS° is positive:**
   - This describes an exothermic process with an increase in system entropy. ΔG° is negative at all temperatures. The forward reaction is always spontaneous under standard conditions.

These scenarios are summarized in Table 10.5.2

Table 10.5.2

ΔH°	ΔS°	ΔG°	Spontaneity of Forward Reaction
–	+	always –	spontaneous (at all temperatures)
+	–	always +	nonspontaneous (at all temperatures)
–	–	– (lower T) + (higher T)	spontaneous at lower temperatures
+	+	+ (lower T) – (higher T)	spontaneous at higher temperatures

Example 10.5.4: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{CO}(g)$$

Does the sign of ΔG° of this process depend upon temperature?

Solution

Combustion processes are exothermic, so $\Delta H^\circ < 0$. This reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^\circ > 0$). $\Delta G^\circ < 0$ is negative at all temperatures, and the forward reaction is always spontaneous.

Exercise 10.5.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s)+3\,\mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{Fe_2O_3}(s)$$

Does the sign of ΔG° of this process depend upon temperature?

Answer available at the end of this section.

For a process in which the sign of ΔG° depends on temperature, there is a specific temperature at which $\Delta G^\circ = 0$. At this point, the system is at equilibrium under standard state conditions. The "higher" and "lower" temperatures mentioned earlier refer to whether the system temperature is above or below this equilibrium temperature. To visualize this, consider a plot of ΔG° vs. T, based on the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

This equation has the same form as a linear function, with an intercept $b = \Delta H^\circ$ a slope $m = -\Delta S^\circ$:

$$y = b + mx$$

Figure 10.5.1 shows this relationship for the four possible combinations of signs for ΔH° and ΔS°:

- Green line: Exothermic ($\Delta H^\circ < 0$) with increasing entropy ($\Delta S^\circ > 0$). ΔG° is negative at all temperatures, so the forward reaction is always spontaneous.
- Red line: Endothermic reaction ($\Delta H^\circ > 0$) with decreasing entropy ($\Delta S^\circ < 0$). ΔG° is positive at all temperatures, so the forward reaction is never spontaneous.
- Yellow lines: ΔH° and ΔS° have the same sign, so ΔG° depends on temperature:
  - For $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$ (upper yellow line), ΔG° is positive at lower temperatures and becomes negative at higher temperatures. The forward reaction becomes spontaneous above a certain temperature.
  - or $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$ (lower yellow line), ΔG° is negative at lower temperatures and becomes positive at higher temperatures. The forward reaction is spontaneous only below a certain temperature.

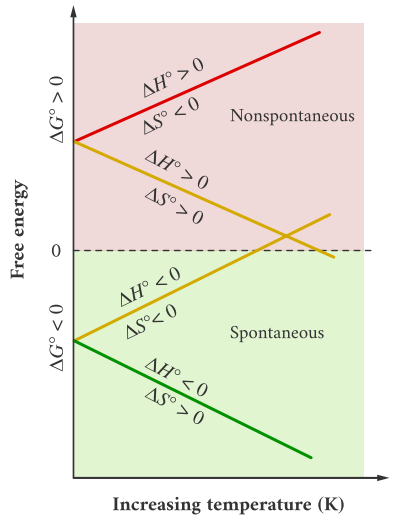


Figure 10.5.1: Plot of standard free energy change (ΔG°) versus temperature (T) for different combinations of enthalpy (ΔH°) and entropy (ΔS°). The green and red lines represent processes where ΔG° is always negative or always positive, respectively, and spontaneity is temperature-independent. The yellow lines show processes where ΔG° changes sign with temperature. The temperature at which each yellow line crosses the x-axis ($\Delta G^\circ = 0$) marks the point where the reaction changes from spontaneous to nonspontaneous, or vice versa, under standard state conditions.

The "cross-over" temperature, the x-intercept of each yellow line, is the temperature at which ΔG° is zero:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

Solving for T:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

This temperature marks the point where the direction of spontaneity changes under standard state conditions.

Using Standard Enthalpy and Entropy Values at Other Temperatures

As long as no phase change occurs, the values of ΔH° and ΔS° typically do not change much with temperature. This allows us to treat them as constants over moderate temperature ranges. We can use the tabulated standard values (typically reported at 298 K) to estimate ΔG° at other temperatures using the expression:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

This approximation is reasonable as long as the temperature range is moderate and no phase transitions (e.g., melting, boiling) occur for any substances involved in the reaction.

Example 10.5.5

Calculate ΔG° at 25°C and at 300°C for the reaction:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

Assume that ΔH° and ΔS° do not change between 25°C and 300°C.

Use these data:

- $S^\circ(\mathrm{N_2})$ = 191.6 J/(mol · K),
- $S^\circ(\mathrm{H_2})$ = 130.7 J/(mol · K),
- $S^\circ(\mathrm{NH_3})$ = 192.8 J/(mol · K)
- $\Delta H_f^\circ(\mathrm{NH_3})$ = –45.9 kJ/mol.

Given: balanced chemical equation, temperatures, ΔS° values, and ΔH_f° for NH_3

Asked for: ΔG° at 25°C and 300°C

Strategy:

A. Calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH_f° for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 10.5.1 to obtain ΔG° for the reaction at 298 K.
C. Assuming that ΔH° and ΔS° are independent of temperature, substitute values into Equation 10.5.1 to obtain ΔG° for the reaction at 300°C.

Solution

A. Calculate ΔS°:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\mathrm{NH_3}) - [S^\circ(\mathrm{N_2}) + 3S^\circ(\mathrm{H_2})] \\ &= [2(192.8\ \mathrm{J/(mol \cdot K)})] - [1(191.6\ \mathrm{J/(mol \cdot K)}) + 3(130.7\ \mathrm{J/(mol \cdot K)})] \\ &= -198.1\ \mathrm{J/(mol \cdot K)})\end{aligned}$$

Calculate ΔH°:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2(-45.9\ \text{kJ/mol})] - [(1(0\ \text{kJ/mol}) + 3(0\ \text{kJ/mol})] \\ &= -91.8\ \text{kJ/mol}\end{aligned}$$

B. Calculate ΔG° at 298 K:

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \Delta H^\circ - T\Delta S^\circ \\ &= \left(-91.8\ \frac{\text{kJ}}{\text{mol}}\right) - (298\ \text{K})\left(-198.1\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right) \\ &= -32.7\ \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

C. Calculate ΔG° at 300°C (573 K):

$$\begin{aligned}\Delta G^\circ &= (-91.8\ \text{kJ/mol}) - (573\ \text{K})(-198.1\ \text{J/(mol}\cdot\text{K)})(1\ \text{kJ/1000 J}) \\ &= 21.7\ \text{kJ/mol}\end{aligned}$$

Changing the temperature has a major effect on the spontaneity of this reaction. At 298 K, the reaction is spontaneous under standard conditions, though in practice it is extremely slow. Although raising the temperature speeds up the reaction (beneficial for kinetics), it also makes the process thermodynamically unfavourable by increasing ΔG°. This tradeoff is central to designing industrial processes like ammonia synthesis.

Exercise 10.5.4

Calculate ΔG° at (a) 25°C and (b) 750 °C for the reaction important in the formation of urban smog:

$$2\,\text{NO}\,(\text{g}) + \text{O}_2\,(\text{g}) \rightleftharpoons 2\,\text{NO}_2\,(\text{g})$$

Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- $S^\circ(\text{NO})$ = 210.8 J/(mol·K),
- $S^\circ(\text{O}_2)$ = 205.2 J/(mol·K),
- $S^\circ(\text{NO}_2)$ = 240.1 J/(mol·K),
- $\Delta H^\circ_f(\text{NO}_2)$ = 33.2 kJ/mol, and
- $\Delta H^\circ_f(\text{NO})$ = 91.3 kJ/mol.

Answer available at the end of this section.

The effect of temperature on the spontaneity of a reaction, which is an important factor in experimental design and industrial processes, depends on both the sign and magnitude of ΔH° and ΔS°. The temperature at which a reaction is at equilibrium under standard state conditions can be calculated by setting ΔG° = 0. This is known as the crossover temperature, the temperature at which a reaction switches from being spontaneous to nonspontaneous (or vice versa) under standard conditions.

Example 10.5.6

Consider the reaction from Example 10.5.5:

$$\text{N}_2\,(\text{g}) + 3\,\text{H}_2\,(\text{g}) \rightleftharpoons 2\,\text{NH}_3\,(\text{g})$$

From the calculations in the earlier example:

ΔS°= -198.1 J/(mol·K)

ΔH°= -91.8 kJ/mol

Because both ΔH° and ΔS° are negative, the reaction is spontaneous at lower temperatures and nonspontaneous at higher temperatures.

Calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 10.5.1 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 10.5.1 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-91.8\ \text{kJ/mol}\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right)}{-198.1\ \text{J/(mol}\cdot\text{K)}} = 463\ \text{K}$$

The reaction is spontaneous under standard state conditions below 463 K and nonspontaneous above 463 K.

This example highlights a key challenge in industrial chemistry: increasing the temperature speeds up the reaction (good for kinetics) but also makes it thermodynamically less favorable (bad for yield). The synthesis of ammonia is thus a classic case of balancing kinetics and thermodynamics.

Exercise 10.5.5

Consider the reaction from Exercise 10.5.4:

$$2\,\text{NO}\,(\text{g}) + \text{O}_2\,(\text{g}) \rightleftharpoons 2\,\text{NO}_2\,(\text{g})$$

From the calculations in the earlier example:

ΔS°= -146.6 J/(mol · K)

ΔH°= -116.2 kJ/mol

Because both ΔH° and ΔS° are negative, the reaction is spontaneous at lower temperatures and nonspontaneous at higher temperatures.

Calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Answer available at the end of this section.

Summary

The change in Gibbs free energy (ΔG), a state function, allows us to predict the spontaneity of a process using only system properties:

$$\Delta G = \Delta H - T\Delta S$$

A negative value of ΔG corresponds to a positive $\Delta S_{\text{universe}}$, indicating a spontaneous process.

In addition to indicating spontaneity, ΔG also tells us the maximum amount of useful work (w) a system can perform:

$$\Delta G = w_{\text{max}}$$

The standard free-energy change (ΔG°) is the change in free energy when all reactants and products are in their standard states (1 M for solutions, 1 atm for gases and pure substances for solids and liquids). The standard free energy of formation (ΔG°_f), is the change in free energy when one mol of a substance in its standard state forms from its elements in their standard states. These values can be used to calculate ΔG° for a reaction:

$$\Delta G^\circ = \sum mG^\circ_f(\text{products}) - \sum nG^\circ_f(\text{reactants})$$

A nonspontaneous reaction ($\Delta G > 0$) can be driven by coupling it to a spontaneous reaction ($\Delta G < 0$), as long as the overall ΔG for the combine process is negative.

The value of ΔG for a reaction depends on temperature. For processes with the same sign of ΔH and ΔS, either an exothermic reaction ($\Delta H < 0$) with a decrease in entropy ($\Delta S < 0$) or an endothermic reaction ($\Delta H > 0$) with an increase in entropy ($\Delta S > 0$), the spontaneity of the reaction is temperature-dependent. In such cases, the temperature at which the reaction switches from spontaneous to nonspontaneous can be found by setting:

$$\Delta G = 0 \Rightarrow T = \frac{\Delta H}{\Delta S}$$

This crossover temperature represents the point where the direction of spontaneity changes under standard state conditions.

Glossary

Gibbs free energy (*G*)
: Thermodynamic property defined in terms of system enthalpy and entropy, allowing the prediction of spontaneity.

Gibbs free energy change (Δ*G*)
: The amount of energy available that can harnessed to do useful work in a thermodynamic system; equal to the sum of the enthalpy plus the product of the temperature and entropy of the system; can predict direction of chemical reaction under constant temperature and pressure.

standard free energies of formation (Δ*G*°*f*)
: The change in free energy accompanying the formation of one mole of substance from its elements in their standard states.

standard free energy change (Δ*G*°)
: The change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions).

Answers

Exercise 10.5.1

$$\begin{aligned}\Delta S^\circ &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})\\ \Delta S^\circ &= S^\circ(\text{N}_2\text{H}_4\,(\text{l})) - [2 \times S^\circ(\text{H}_2\,(\text{g})) + S^\circ(\text{N}_2\,(\text{g}))]\\ &= 121.2\ \text{J/(mol}\cdot\text{K)} - [2(130.7\ \text{J/(mol}\cdot\text{K))} + 191.6\ \text{J/(mol}\cdot\text{K)}]\\ &= -331.8\ \text{J/(mol}\cdot\text{K)}\end{aligned}$$

The change in entropy is negative as expected because there are gases present in the reactants and not in the products.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ &= 50.6\ \text{kJ/mol} - (298.15\ \text{K})\left(-331.8\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\left(\frac{\text{kJ}}{1000\ \text{J}}\right)\\ &= 149.5\ \text{kJ/mol}\end{aligned}$$

ΔG° is positive so the reaction is non spontaneous in the forward direction (the reverse reaction is spontaneous) under standard state conditions.

Because the reaction is endothermic and the entropy change is negative, the free energy change is positive at all temperatures, so the reaction is never spontaneous under standard conditions.

Exercise 10.5.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ &= \sum mG_f^\circ(\text{ products }) - \sum n\Delta G_f^\circ(\text{ reactants }) \\ &= \left[1\Delta G_f^\circ\left(\mathrm{H_2(g)}\right) + 1\Delta G_f^\circ\left(\mathrm{C_2H_2(g)}\right)\right] - 1\Delta G_f^\circ\left(\mathrm{C_2H_4(g)}\right) \\ &= [1(0\text{ kJ/mol}) + 1(209.9\text{ kJ/mol})] - 1(68.4\text{ kJ / mol}) = 141.5\text{ kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ &= \sum m\Delta H_f^\circ(\text{ products }) - \sum n\Delta H_f^\circ(\text{ reactants }) \\ &= \left[1\Delta H_f^\circ\left(\mathrm{H_2(g)}\right) + 1\Delta H_f^\circ\left(\mathrm{C_2H_2(g)}\right)\right] - 1\Delta H_f^\circ\left(\mathrm{C_2H_4(g)}\right) \\ &= [1(0\text{ kJ/mol}) + (227.4\text{ kJ/mol})] - 1(52.4\text{ kJ/mol}) = 175.0\text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum m\Delta S^\circ(\text{ products }) - \sum n\Delta S^\circ(\text{ reactants }) \\ &= [1\ \Delta S^\circ\left(\mathrm{H_2(g)}\right) + 1\Delta S^\circ\left(\mathrm{C_2H_2(g)}\right)] - 1\Delta S^\circ\left(\mathrm{C_2H_4(g)}\right) \\ &= [1(130.7\text{ J /(mol·K)}) + 1(200.9\text{ J/(mol·K)})] - 1(219.3\text{ J/(mol·K)}) = 112.3\text{ J/(mol·K)}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 175.0\text{ kJ} - (298.15\text{ K})(112.3\text{ J/(mol·K)})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right) \\ &= 141.5\text{ kJ/mol}\end{aligned}$$

ΔG° is positive, so the reaction is nonspontaneous under standard state conditions at 25°C.

Exercise 10.5.3

Since the reaction generates heat, ΔH° is negative. ΔS° is negative because gas is consumed in the reaction. ΔG° will be negative at lower temperatures.

Exercise 10.5.4

Calculate ΔS°:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\mathrm{NO_2}) - [2S^\circ(\mathrm{NO}) + 1S^\circ(\mathrm{O_2})] \\ &= [2(240.1\text{ J/(mol}\cdot\text{K)})] - [2(210.8\text{ J/(mol}\cdot\text{K)}) + 1(205.2\text{ J/(mol}\cdot\text{K)})] \\ &= -146.6\text{ J/(mol}\cdot\text{K)})\end{aligned}$$

Calculate ΔH°:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_{\text{f}}(\mathrm{NO_2}) - [2\Delta H^\circ_{\text{f}}(\mathrm{NO}) + 1\Delta H^\circ_{\text{f}}(\mathrm{O_2})] \\ &= [2(33.2\text{ kJ/mol})] - [(2(91.3\text{ kJ/mol}) + 1(0\text{ kJ/mol})] \\ &= -116.2\text{ kJ/mol}\end{aligned}$$

Calculate ΔG° at 25°C (298 K):

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-116.2\text{ kJ/mol}) - (298\text{ K})(-146.6\text{ J/(mol K)})(1\text{ kJ}/1000\text{ J}) = -72.5\text{ kJ/mol}$$

Calculate ΔG° at 750°C (1023 K):

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-116.2\text{ kJ/mol}) - (1023\text{ K})(-146.6\ J/(mol\cdot K))(1\text{ kJ}/1000\text{ J}) = 33.8\text{ kJ/mol}$$

Exercise 10.5.5

The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 10.5.1 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-116.2\text{ kJ/mol}\left(\frac{1000\text{ J}}{1\text{ kJ}}\right)}{-146.6\text{ J/(mol}\cdot\text{K)}} = 792.6\text{ K}$$

At temperatures below 793 K, the forward reaction is spontaneous under standard conditions. At higher temperatures, the reverse reaction becomes spontaneous.

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10.6: Free Energy, Equilibrium, and Non-Standard State Conditions

Learning Objectives

- Relate the standard free energy change (ΔG°) to the equilibrium constant (K), and perform calculations using their mathematical relationship.
- Define and distinguish between free energy (ΔG), standard free energy (ΔG°), the equilibrium constant (K), and the reaction quotient (Q).
- Interpret free energy changes under standard and nonstandard conditions to predict spontaneity and equilibrium position.
- Analyze a graph of free energy versus reaction progress to determine direction of spontaneity and equilibrium composition.

Two main criteria help us predict whether a reaction will proceed spontaneously:

1. $\Delta S_{\text{univ}} > 0$,
2. $\Delta G_{\text{sys}} < 0$ (at constant temperature and pressure)

As discussed in Chapter 7, the direction a reaction proceeds also depends on the relationship between the reaction quotient (Q) and the equilibrium constant (K). Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, the system is at equilibrium, and no net change occurs in the concentrations of reactants and products. Table $10.6.1$ summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table $10.6.1$*: Criteria for the Spontaneity of a Process*

Spontaneous	Equilibrium	Nonspontaneous (Spontaneous in reverse)
$\Delta S_{\text{univ}} > 0$	$\Delta S_{\text{univ}} = 0$	$\Delta S_{\text{univ}} < 0$
$\Delta G_{\text{sys}} < 0$	$\Delta G_{\text{sys}} = 0$	$\Delta G_{\text{sys}} > 0$
$Q < K$	$Q = K$	$Q > K$

Because all three criteria assess the same property, spontaneity, there must be a mathematical relationship connecting them. In this section, we'll explore the connection between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Free Energy Change Under Any Condition

The free energy change, ΔG, can be thought of as a measure of the driving force of a process. A negative ΔG represents a driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate (the system is at equilibrium). The sign of ΔG tells us the direction in which the reaction will proceed to reach equilibrium, while the magnitude of ΔG indicates how far the system is from equilibrium under the current conditions. When the reaction quotient Q differs significantly from the equilibrium constant K, the system is far from equilibrium, and the free energy change is large. When Q is close to K, the system is near equilibrium and the free energy change is small. The magnitude of ΔG changes as the reaction progresses and until equilibrium is reached ($Q = K$ and $\Delta G = 0$). This indicates that a reaction being spontaneous under a certain set of initial conditions does not necessarily result in a complete conversion of reactants to products.

For reactions under nonstandard conditions (i.e., concentrations or pressures different from 1 M or 1 atm), the free energy change (ΔG) is related to the standard free energy (ΔG°) change by the equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

In this equation:

- R is the gas constant (8.314 J/mol·K),
- T is temperature in Kelvin,
- Q the reaction quotient at current conditions (Q_p for gases, Q_c for solutions).

This equation allows us to calculate ΔG and determine spontaneity under any set of conditions, as shown in Example 10.6.1.

Example 10.6.1: Calculating ΔG under Nonstandard Conditions

What is the free energy change, ΔG, for the reaction:

$$2\,\mathrm{NH_3\,(g)} \rightleftharpoons 3\,\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)}$$

under the following conditions?

- $T = 25^\circ C$,
- $P_{\mathrm{N_2}} = 0.870\ \mathrm{atm}$
- $P_{\mathrm{H_2}} = 0.250\ \mathrm{atm}$
- $P_{\mathrm{NH_3}} = 12.9\ \mathrm{atm}$
- $\Delta G^\circ = 33.0\ \mathrm{kJ/mol}$

Solution

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= 33.0\frac{\mathrm{kJ}}{\mathrm{mol}} + \left(8.314\frac{\mathrm{J}}{\mathrm{mol\ K}}\right)\left(\frac{\mathrm{kJ}}{1000\ \mathrm{J}}\right)(298\ \mathrm{K}) \ln\left(\frac{((0.250)^3)(0.870)}{(12.9)^2}\right) \\ &= 9.68\ \mathrm{kJ/mol}\end{aligned}$$

Since ΔG is positive, the reaction is nonspontaneous under these conditions. The system will shift toward reactants to move toward equilibrium.

Exercise 10.6.1

What is the free energy change, ΔG, for the reaction:

$$2\,\mathrm{NH_3\,(g)} \rightleftharpoons 3\,\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)}$$

at 25 °C, under the following conditions:

Given:

- $P_{\mathrm{NH_3}} = 0.200\ \mathrm{atm}$
- $P_{\mathrm{H_2}} = 0.0100\ \mathrm{atm}$
- $P_{\mathrm{N_2}} = 0.0100\ \mathrm{atm}$
- $\Delta G^\circ = 33.0\ \mathrm{kJ/mol}$

Is the reaction spontaneous under these conditions?

Answer available at the end of this section.

Free Energy and Equilibrium

We've learned that ΔG represents the free energy change under any conditions, while ΔG° refers to the free energy change

under standard conditions (1 atm for gases, 1 M for solutes). Because standard conditions are fixed, ΔG° is a constant for a given reaction at a given temperature. This makes it possible to relate ΔG° to another constant: the equilibrium constant, K. The sign and magnitude of ΔG° reveal how far a reaction will shift to reach equilibrium and whether products or reactants will dominate once equilibrium is established.

We've also seen that the sign of ΔG° indicates the direction of spontaneity under standard conditions. When $\Delta G^\circ < 0$, the reaction proceeds spontaneously in the forward direction, favouring the products. At equilibrium, products will be present in larger amounts than reactants, and the equilibrium constant K must be greater than 1.

Similarly, when $\Delta G^\circ > 0$, the reaction is spontaneous in the reverse direction. This leads to greater concentrations or pressures of the reactants at equilibrium and smaller values for the products, meaning $K < 1$.

We can express the connection between ΔG° and K mathematically. At equilibrium, the reaction quotient Q equals the equilibrium constant K, and the free energy change ΔG is zero. Substituting into the general equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

gives:

$$0 = \Delta G^\circ + RT \ln K \quad (\text{at equilibrium})$$

Rearranging:

$$\Delta G^\circ = -RT \ln K$$

or equivalently:

$$K = e^{-\frac{\Delta G^\circ}{RT}}$$

This important relationship links two core thermodynamic concepts: standard free energy change and the equilibrium constant. It allows us to calculate one from the other and to interpret equilibrium composition in thermodynamic terms.

Table 10.6.2: Relationship Between Standard Free Energy (ΔG°), Equilibrium Constant (K), and Equilibrium Composition

K	ΔG°	**Equilibrium Composition**
> 1	< 0	Products predominate at equilibrium
< 1	> 0	Reactants predominate at equilibrium
$= 1$	$= 0$	Reactants and products are equally present

Example 10.6.2: Calculating an Equilibrium Constant using Standard Free Energy Change

Given the following standard free energies of formation at 25 °C:

- $\Delta G_f^\circ(\text{Ag}^+(aq)) = 77.1 \text{ kJ/mol}$
- $\Delta G_f^\circ(\text{Cl}^-(aq)) = -131.2 \text{ kJ/mol}$
- $\Delta G_f^\circ(\text{AgCl}(s)) = -109.8 \text{ kJ/mol}$

Calculate the solubility product constant, K_{sp}, for the dissolution of silver chloride:

$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$

Solution

Step 1: Calculate the standard free energy change for the reaction:

$$\begin{aligned}\Delta G^\circ &= \left[\Delta G_f^\circ(\mathrm{Ag^+}) + \Delta G_f^\circ(\mathrm{Cl^-})\right] - \Delta G_f^\circ(\mathrm{AgCl}) \\ &= [77.1\ \mathrm{kJ/mol} + (-131.2\ \mathrm{kJ/mol})] - (-109.8\ \mathrm{kJ/mol}) \\ &= -54.1\ \mathrm{kJ/mol} + 109.8\ \mathrm{kJ/mol} = 55.7\ \mathrm{kJ/mol}\end{aligned}$$

Step 2: Use the relationship $\Delta G^\circ = -RT\ln K$ to solve for K_{sp}:

$$\begin{aligned}K_{\mathrm{sp}} &= e^{-\frac{\Delta G^\circ}{RT}} \\ &= e^{-\frac{55.7\times10^3\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol\cdot K}\times 298.15\ \mathrm{K}}} \\ &= e^{-22.470} = 1.74\times10^{-10}\end{aligned}$$

The value of K_{sp} is very small, meaning that only a small amount of $\mathrm{AgCl(s)}$ dissolves at equilibrium. This is consistent with the relatively large, positive value of ΔG°.

Exercise 10.6.2

Calculate the equilibrium constant (K) for the dissociation of dinitrogen tetroxide at 25 °C:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)}$$

- $\Delta G_f^\circ(\mathrm{N_2O_4}(g)) = 97.5\ \mathrm{kJ/mol}$
- $\Delta G_f^\circ(\mathrm{NO_2}(g)) = 51.3\ \mathrm{kJ/mol}$

Answer available at the end of this section.

Example 10.6.3

At 25 °C, the equilibrium constant for the reaction:

$$\mathrm{CO}(g)+\mathrm{Cl_2}(g) \rightleftharpoons \mathrm{COCl_2}(g)$$

is $K = 1.5\times10^3$. Calculate the standard free energy change ΔG° for the reaction at this temperature.

Solution

Use the relationship:

$$\Delta G^\circ = -RT\ln K$$

Substitute values:

$$\begin{aligned}\Delta G^\circ &= -(8.314\ \mathrm{J/mol\cdot K})(298.15\ \mathrm{K})\ln(1.5\times10^3) \\ &= -18125\ \mathrm{J/mol} \\ &= -18.1\ \mathrm{kJ/mol}\end{aligned}$$

Exercise 10.6.3

At 25 °C, the equilibrium constant for the reaction:

$$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\,\mathrm{HOCl}(g)$$

is $K = 0.0900$. Calculate the standard free energy change ΔG° for the reaction at this temperature.

Answer available at the end of this section.

Free Energy Diagrams and Equilibrium Position

The diagrams below (Figure $10.6.1$) show how the Gibbs free energy of a reaction mixture changes as it shifts from any initial composition toward equilibrium. Each curve represents a reaction with a different standard free energy change, ΔG°, and therefore a different equilibrium constant, K. The minimum of each curve represents the equilibrium point, where $\Delta G = 0$ and $Q = K$.

Each point along the curve corresponds to a different composition of the reaction mixture (i.e., different values of Q). The slope at any point corresponds to the value of ΔG and indicates the direction of spontaneous change:

- If the system starts to the left of equilibrium (mostly reactants, $Q < K$), then the slope is negative ($\Delta G < 0$) and the reaction proceeds spontaneously in the forward direction.
- If the system starts to the right of equilibrium (mostly products, $Q > K$), then the slope is positive ($\Delta G > 0$) and the reaction proceeds spontaneously in the reverse direction.

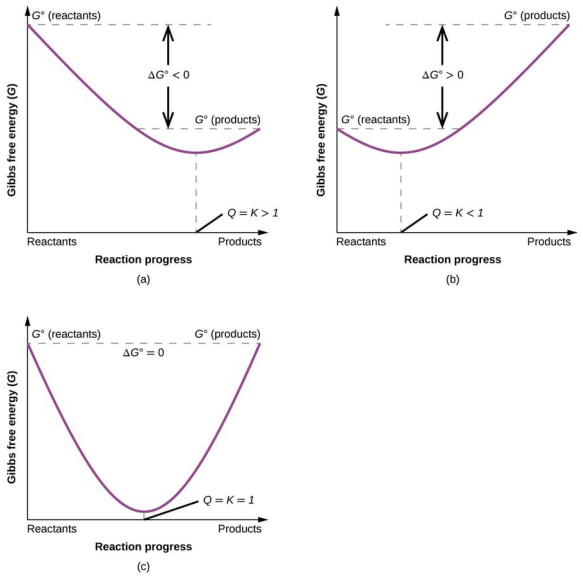
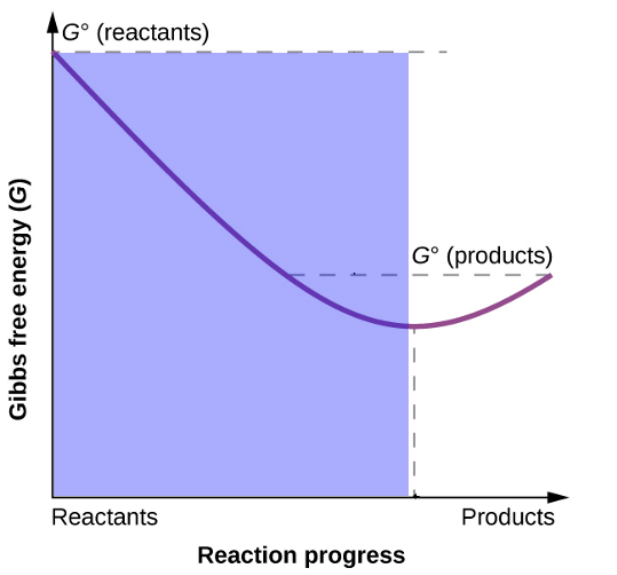


Figure $10.6.1$: Gibbs free energy curves for three different reactions: (a) $\Delta G^\circ < 0$: Products are lower in free energy than reactants. The reaction is product-favoured, and $K > 1$. (b) $\Delta G^\circ > 0$: Reactants are lower in free energy than products. The reaction is reactant-favoured, and $K < 1$. (c) $\Delta G^\circ = 0$: Reactants and products have equal free energy under standard conditions. This is a special case where the reactants and products are equally favoured and $K = 1$. In all cases, a nonequilibrium system will proceed spontaneously in the direction that minimizes free energy and establishes equilibrium.

These diagrams illustrate a key idea: the free energy change, ΔG, tells us both the direction a reaction mixture will shift and how far it is from equilibrium. When Q differs significantly from K, ΔG is large and the system undergoes a substantial change in its free energy as it moves toward equilibrium. When Q is close to K, the system is already near equilibrium, and only a small change of free energy is involved in the spontaneous reaction to equilibrium.

Example 10.6.4

Consider the following free energy diagram for the reaction $\mathrm{A(g)} \rightleftharpoons \mathrm{B(g)}$:



a) What is the relationship between Q and K in the shaded region of the diagram?

b) What is the sign of ΔG° for the reaction?

c) At equilibrium, which species, $\mathrm{A(g)}$ or $\mathrm{B(g)}$, has the higher pressure?

d) Suppose a sample of pure $\mathrm{B(g)}$ is placed into an empty container. What happens as the system approaches equilibrium? What is the sign of ΔG for the initial change?

Solution

a) The shaded region has more reactant and less product than at equilibrium, so $Q < K$. This means the reaction will proceed spontaneously in the forward direction to reach equilibrium.

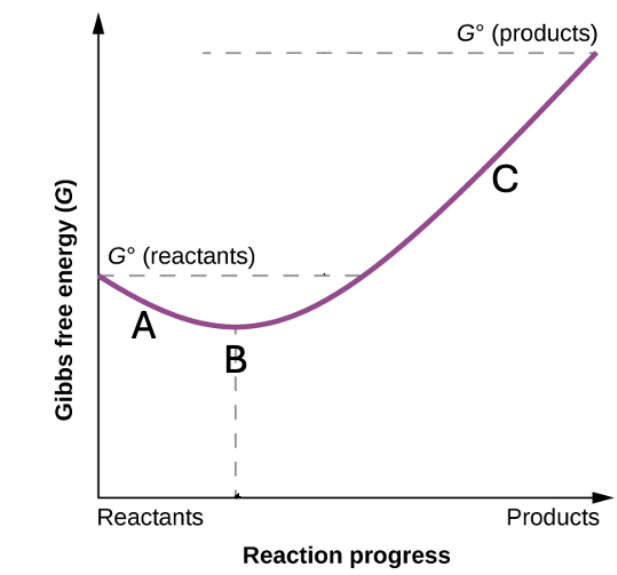
b) ΔG° is the free energy change when reactants and products are both present at 1 atm (standard state). From the diagram, the standard free energy of the products is lower than that of the reactants, so ΔG° is negative. The reaction is product-favoured and $K > 1$.

c) Since the free energy minimum (equilibrium point) lies closer to the product side of the curve, the system contains more $\mathrm{B(g)}$ at equilibrium than $\mathrm{A(g)}$, so $\mathrm{B(g)}$ has a higher pressure.

d) If the system contains only $\mathrm{B(g)}$, $Q > K$ and the reaction will proceed spontaneously in the reverse direction to form $\mathrm{A(g)}$ until equilibrium is established. In this case $\Delta G > 0$ for the forward direction, meaning the reverse reaction is spontaneous.

Exercise 10.6.4

Consider the following free energy diagram for the reaction $\mathrm{D(g)} \rightleftharpoons \mathrm{E(g)}$:



(a) What is the sign of ΔG at point A? In which direction does the reaction proceed to reach equilibrium?

(b) What is the sign of ΔG at point B? In which direction does the reaction proceed to reach equilibrium?

(c) What is the sign of ΔG at point C? In which direction does the reaction proceed to equilibrium?

(d) What is the sign of ΔG° for the reaction?

(e) Is $K > 1$, $K < 1$, or $K = 1$?

Answer available at the end of this section.

Summary

Gibbs free energy change, ΔG, is a key thermodynamic quantity that tells us both the direction a reaction will shift and how far the system is from equilibrium.

- ΔG is the free energy change under any conditions. It depends on the current composition of the reaction mixture.
- ΔG° is the standard free energy change: the value of ΔG when all reactants and products are at 1 atm or 1 M concentration.
- Q is the reaction quotient, which reflects the relative amounts of reactants and products at a specific moment.
- K is the equilibrium constant. It represents the value of Q at equilibrium and depends only on temperature.

These quantities are related by the following equations:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium, ΔG = 0 and $Q = K$, so $\Delta G^\circ = -RT \ln K$

The sign of ΔG tells us which direction the system will shift to reach equilibrium, while its magnitude indicates how far from equilibrium the system currently is.

Free Energy and Reaction Direction (Any Conditions)

Q vs. K	ΔG	Direction of Reaction	Spontaneity
$Q < K$	$\Delta G < 0$	Forward (→ products)	In forward direction

Q vs. K	ΔG	Direction of Reaction	Spontaneity
$Q = K$	$\Delta G = 0$	No net change	In both directions
$Q > K$	$\Delta G > 0$	Reverse ($\rightarrow$ reactants)	In reverse direction

What Does ΔG° Tell You?

ΔG°	K	Equilibrium Position
< 0	$K > 1$	Products favored
$= 0$	$K = 1$	Reactants and products equally present
> 0	$K < 1$	Reactants favored

Answers

Exercise 10.6.1

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= 33.0\frac{\text{kJ}}{\text{mol}} + \left(8.314\frac{\text{J}}{\text{mol K}}\right)\left(\frac{\text{kJ}}{1000\text{ J}}\right)(298\text{ K})\ln\left(\frac{((0.0100)^3)(0.0100)}{(0.200)^2}\right) \\ &= -4.7\text{ kJ/mol}\end{aligned}$$

The reaction is spontaneous under these conditions.

Exercise 10.6.2

$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ(\text{NO}_2\,(\text{g})) - \Delta G_f^\circ(\text{N}_2\text{O}_4\,(\text{g})) \\ &= 2(51.3\text{ kJ/mol}) - 97.5\text{ kJ/mol} \\ &= 5.10\text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}K_{\text{sp}} &= e^{-\frac{\Delta G^\circ}{RT}} \\ &= e^{-\frac{5.10\times10^3\text{ J/mol}}{(8.314\text{ J/mol·K})(298.15\text{ K})}} \\ &= e^{-2.06} = 0.128\end{aligned}$$

In this case ΔG° is small and positive, so K is smaller than 1 as expected.

Exercise 10.6.3

$$\begin{aligned}\Delta G^\circ &= -(8.314\text{ J/mol·K})(298.15\text{ K})\ln(0.0900) \\ &= 5969\text{ J/mol} \\ &= 5.97\text{ kJ/mol}\end{aligned}$$

Exercise 10.6.4

(a) At point A, the system contains mostly reactants. Since this point is to the left of equilibrium, $\Delta G < 0$, and the reaction proceeds spontaneously in the forward direction to form more product.

(b) Point B is at the minimum of the curve, where the free energy is lowest. This represents the equilibrium composition, so $\Delta G = 0$, and no net change occurs.

(c) At point C, the system contains mostly products. This point is to the right of equilibrium, so $\Delta G > 0$, and the reaction proceeds spontaneously in the reverse direction to form more reactants.

(d) From the diagram, the standard free energy of the products is higher than that of the reactants. Therefore, $\Delta G^\circ > 0$, meaning the reaction is reactant-favored under standard conditions.

(e) Since $\Delta G^\circ > 0$, the equilibrium constant $K < 1$. This means the reactants are more abundant than the products at equilibrium.

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10.7: Phase Transitions and Phase Diagrams

Learning Objectives

- Describe phase transitions in terms of enthalpy, entropy and free energy.
- Explain how temperature affects the spontaneity of a phase change and perform related calculations.
- Describe vapour pressure and its relationship to temperature and the strength of intermolecular forces.
- Relate the phase of a substance to the balance between kinetic energy (temperature) and intermolecular forces.
- Interpret a heating or cooling curve for a pure substance.
- Identify regions, phase boundaries, the triple point, and the critical point on a phase diagram.
- Use a phase diagram to predict the physical state of a substance at various temperatures and pressures.

Many of us have boiled water to cook or noticed that the water level in a glass left on a desk decreases over time. These are everyday examples of phase changes, where a substance transitions between solid, liquid, and gas. In this section, we'll explore the thermodynamics of phase changes. Along the way, we'll bring together ideas we've already encountered — including enthalpy, entropy, free energy, and equilibrium — to see how they work together to explain when and why a phase change occurs, and how the phase of a substance depends on temperature. We'll also connect this macroscopic view to a molecular one by examining how kinetic energy distributions help explain particle behaviour during phase transitions.

Enthalpy and Entropy of Phase Changes

Phase changes are always accompanied by a change in the energy of a system. For example, converting a liquid, where the molecules are close together, to a gas, where the molecules are on average far apart, requires an input of energy. This energy (in the form of heat) increases the kinetic energy of the molecules, allowing them to overcome the intermolecular forces holding them in the liquid phase. In general:

- Transitions that move particles farther apart (solid → liquid → gas) require energy to overcome intermolecular forces ($\Delta H > 0$).
- Transitions that bring particles closer together (gas → liquid → solid) release energy as intermolecular attractions increase ($\Delta H < 0$).

These enthalpy changes are shown in Figure $10.7.1$.

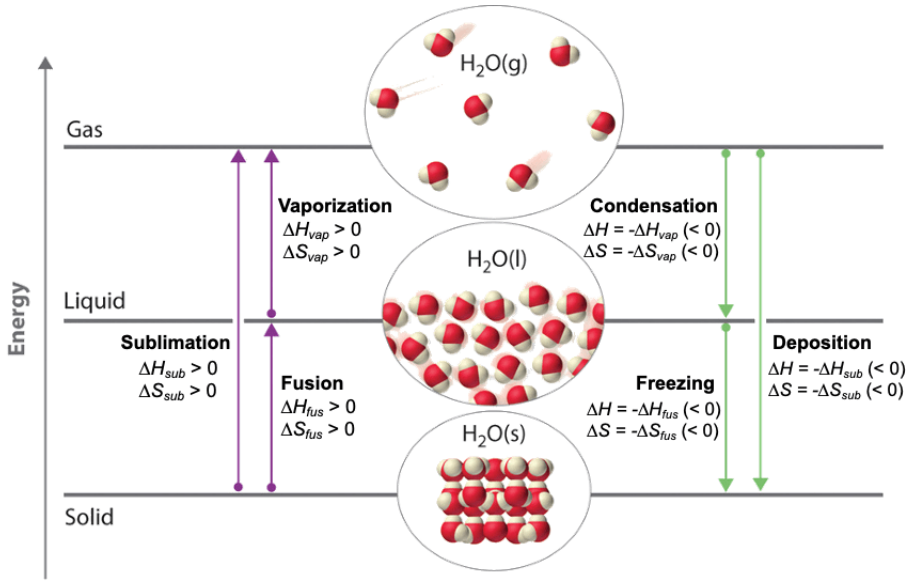


Figure 10.7.1 Enthalpy and entropy changes that accompany phase transitions. Purple arrows represent transitions in which energy is absorbed (solid → liquid, liquid → gas, solid → gas). Green arrows represent transitions in which energy is released (gas → liquid, liquid → solid, gas → solid). (CC BY-SA-NC; modified from anonymous)

As we saw earlier in this chapter, phase changes are also accompanied by changes in entropy. Solids have the lowest entropy because their particles are fixed in place and have limited freedom of motion. Liquids have more entropy, as their particles are still close together but can move past one another. Gases have the greatest entropy because their particles are far apart and move freely throughout the container.

Therefore:

- Transitions that move particles farther apart (solid → liquid → gas) result in an increase in entropy ($\Delta S > 0$).
- Transitions that bring particles closer together (gas → liquid → solid) result in a decrease in entropy ($\Delta S < 0$).

These entropy changes are also summarized in Figure 10.7.1.

For each phase transition, the sign of ΔH and ΔS are the same. For instance, vaporization is endothermic ($\Delta H > 0$) and increases entropy ($\Delta S > 0$). This combination means the spontaneity of vaporization depends on temperature, a concept we see in everyday life. Water boils spontaneously at temperatures above 100 °C, but condenses spontaneously below that temperature. The spontaneity of all phase changes depends on temperature. Melting, sublimation, freezing, and deposition are all governed by the balance of enthalpy and entropy. We'll explore this relationship more closely using the free energy equation.

Temperature and Spontaneity of Phase Changes

We can predict whether a phase change is spontaneous at a given temperature using the Gibbs free energy equation:

$$\Delta G = \Delta H - T\Delta S$$

For vaporization (and other phase changes that move particles farther apart), both ΔH and ΔS are positive. This means the sign of ΔG depends on the temperature:

- At lower temperatures, the $T\Delta S$ term is small, so $\Delta G > 0$ and the process is nonspontaneous.
- At higher temperatures, the $T\Delta S$ term becomes large, so $\Delta G < 0$ and the process becomes spontaneous.

The temperature at which $\Delta G = 0$ is the point where the two phases are in equilibrium. For vaporization, this is the boiling point. Below this temperature, condensation is spontaneous; above it, vaporization is spontaneous. At this transition temperature, both condensation and vaporization are both spontaneous and happen at the same rate.

We can calculate this temperature by solving for T when $\Delta G = 0$:

$$0 = \Delta H_{\text{vap}} - T_{\text{boil}}\Delta S_{\text{vap}} \quad \Rightarrow \quad T_{\text{boil}} = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}}$$

Example 10.7.1

Consider the vaporization of water:

$$\text{H}_2\text{O}\,(\text{l}) \rightleftharpoons \text{H}_2\text{O}\,(\text{g})$$

Given the following thermodynamic data at 298 K:

Substance	ΔH_f° (kJ/mol)	S° (J/mol·K)
$\text{H}_2\text{O}\,(\text{l})$	–285.8	70.0
$\text{H}_2\text{O}\,(\text{g})$	–241.8	188.8

a. Calculate $\Delta H_{\text{vap}}^\circ$.
b. Calculate $\Delta S_{\text{vap}}^\circ$.
c. What is $\Delta G_{\text{vap}}^\circ$ at 298 K? Is vaporization spontaneous under standard conditions at 298 K?
d. What is the boiling point of water under standard state conditions? (i.e. at what temperature does vaporization become spontaneous?) Assume ΔH° and ΔS° do not change with temperature.

Solution

a.

$$\Delta H_{\text{vap}}^\circ = \Delta H_f^\circ(\text{H}_2\text{O}\,(\text{g})) - \Delta H_f^\circ(\text{H}_2\text{O}\,(\text{l})) = -241.8\ \text{kJ/mol} - (-285.8\ \text{kJ/mol}) = 44.0\ \text{kJ/mol}$$

b.

$$\Delta S_{\text{vap}}^\circ = S^\circ(\text{H}_2\text{O}\,(\text{g})) - S^\circ(\text{H}_2\text{O}\,(\text{l})) = 188.8\ \text{J/mol·K} - 70.0\ \text{J/mol·K} = 118.8\ \text{J/mol·K}$$

c.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 44.0\ \text{kJ/mol} - (298\ \text{K})(118.8\ \text{J/mol·K})\left(\frac{\text{kJ}}{1000\ \text{J}}\right) = 8.6\ \text{kJ/mol}$$

Since $\Delta G^\circ > 0$, vaporization is not spontaneous under standard state conditions at 298 K.

d. To find the temperature where $\Delta G^\circ = 0$, solve:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.0\ \text{kJ/mol}}{118.8\ \text{J/mol·K}} \cdot \left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right) = 370\ \text{K}$$

The calculated boiling point (370 K or 97 °C) is slightly lower than the actual value of 100 °C because the thermodynamic values used are tabulated at 25 °C (298 K), not at the boiling point. In reality, both $\Delta H_{\text{vap}}^\circ$ and $\Delta S_{\text{vap}}^\circ$ vary with temperature. Assuming they remain constant is a useful approximation over small temperature ranges.

This same relationship applies to all phase transitions. For melting, the temperature where $\Delta G = 0$ is the melting point. For sublimation, it defines the temperature where solid and gas are in equilibrium. The free energy equation helps us understand why phase changes happen only under certain conditions and why temperature plays such a central role.

Exercise 10.7.1

Figure 10.7.2 shows the sublimation of iodine:

$$\text{I}_2\,(\text{s}) \rightleftharpoons \text{I}_2\,(\text{g})$$



Figure 10.7.2: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Given the following thermodynamic data:

Substance	$\Delta H_f^\circ\ (\mathrm{kJ/mol})$	$S^\circ\ (\mathrm{J/mol{\cdot}K})$
$\mathrm{I_2\,(s)}$	0	116.1
$\mathrm{I_2\,(g)}$	64.4	260.7

a. Calculate $\Delta H^\circ_{\mathrm{sub}}$.
b. Calculate $\Delta S^\circ_{\mathrm{sub}}$.
c. What is $\Delta G^\circ_{\mathrm{sub}}$ at 298 K? Is sublimation spontaneous under standard conditions at 298 K?
d. At what temperature does sublimation become spontaneous? (Assume ΔH° and ΔS° do not change with temperature.)

Answer available at the end of this section.

Vapour Pressure and Phase Equilibrium

When a liquid is placed in a closed container, some molecules at the surface will escape into the gas phase. At the same time, gas-phase molecules can collide with the surface and re-enter the liquid. Over time, these two processes balance, and the system reaches dynamic equilibrium (Figure 10.7.3). At equilibrium, molecules continue to evaporate and condense, but there is no net change in the amount of liquid or vapour. The pressure exerted by the vapour at this point is called the vapour pressure of the liquid. Vapour pressure depends only on the identity of the substance and the temperature, not on the amount of liquid or the size of the container (as long as some liquid is present).

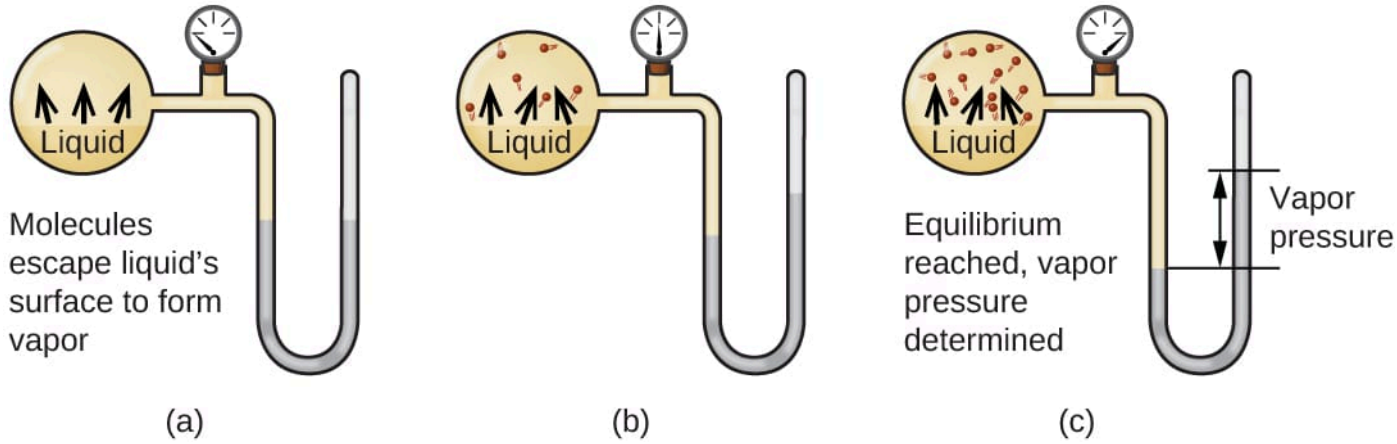


Figure 10.7.3: In a closed container, dynamic equilibrium is reached when (a) molecules escape from the liquid into the gas, (b) the vapour concentration increases, and eventually (c) the rate of condensation equals the rate of evaporation. At this point, the vapour pressure becomes constant.

Even below the boiling point, some vaporization still occurs, and we can treat this as an equilibrium process:

$$\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_2O\,(g)} \quad \Delta G^\circ = 8.6\ \mathrm{kJ/mol\ at\ 298\ K}$$

Using the relationship:

$$\Delta G^\circ = -RT \ln K$$

we can calculate the equilibrium constant K_p, which equals the partial pressure of water vapour:

$$K = e^{-\left(\frac{8.6\ \mathrm{kJ/mol}}{\left(8.314\frac{\mathrm{J}}{\mathrm{mol\ K}}\right)(298\ \mathrm{K})}\right)\left(\frac{1000\ \mathrm{J}}{\mathrm{kJ}}\right)} = 0.031$$

$$K_p = P_{\mathrm{H_2O\,(g)}} = 0.031\ \mathrm{atm} = 23.6\ \mathrm{mmHg}$$

This calculated value matches the known vapour pressure of water at 25 °C, reinforcing the idea that vapour pressure reflects a dynamic equilibrium between the liquid and vapour phases, even well below the boiling point. This also explains why the water level in a forgotten glass slowly drops over time: vaporization continues at room temperature, even though boiling is not occurring.

The same principles apply to a solid in equilibrium with its vapour (sublimation).

Factors Affecting Vapour Pressure

Because vaporization is an endothermic process (it requires energy to overcome intermolecular forces), increasing the temperature increases the rate of evaporation. At higher temperatures, more molecules have enough kinetic energy to escape into the gas phase, shifting the equilibrium to the right. As a result, vapour pressure increases with temperature.

$$\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_2O\,(g)}$$

We can understand this temperature dependence in several ways:

1. Le Châtelier's Principle: Heating the system favours the endothermic direction (vaporization), increasing the vapour pressure until a new equilibrium is reached.
2. Free energy: For a process like vaporization where $\Delta H > 0$ and $\Delta S > 0$, increasing temperature increases the $T\Delta S$ term, making ΔG more negative and favouring the forward direction (vaporization).
3. Molecular perspective: As temperature increases, the kinetic energy of the particles increases, so a greater fraction of molecules will have sufficient energy to overcome the intermolecular forces and escape the liquid (Figure 10.7.4).

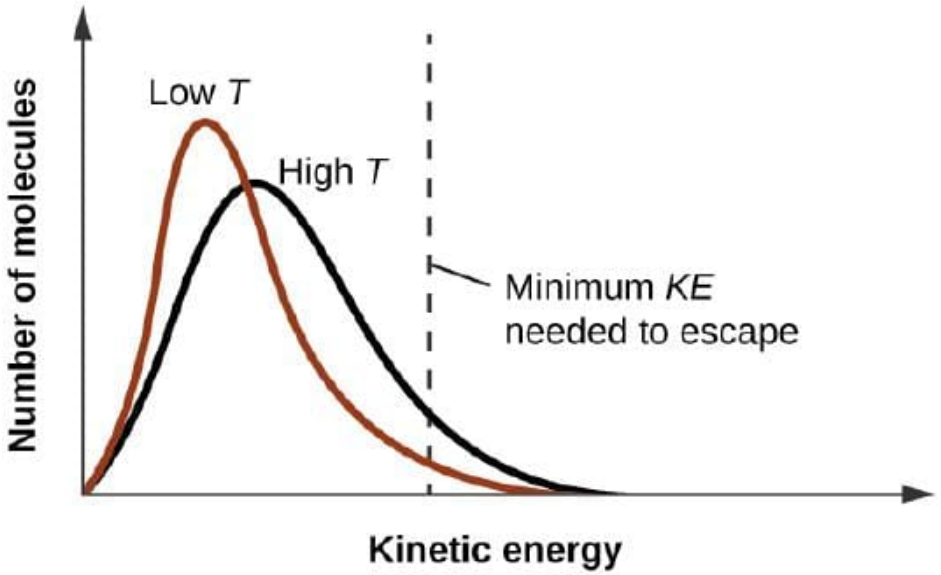


Figure 10.7.4: Temperature affects the distribution of kinetic energies for the molecules in a liquid. At higher temperatures, a greater fraction of molecules have enough energy to escape into the gas phase.

These explanations are not independent. Rather, they describe the same underlying phenomenon differently: increasing temperature shifts the liquid–vapour equilibrium toward the gas phase.

Example 10.7.2

Calculate the vapour pressure of water at 325 K, given the following thermodynamic data:

$$\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_2O\,(g)}$$

$\Delta H^\circ_{\text{vap}} = 44.0\ \text{kJ/mol}, \quad \Delta S^\circ_{\text{vap}} = 118.8\ \text{J/mol·K}$

Assume these values are constant with temperature.

a. Calculate ΔG° for vaporization at 325 K.
b. Calculate the equilibrium constant K_p and the corresponding vapour pressure of water at 325 K.

Solution

a.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.0\ \text{kJ/mol} - (325\ \text{K})(118.8\ \text{J/mol·K})\left(\frac{\text{kJ}}{1000\ \text{J}}\right) = 5.4\ \text{kJ/mol}\end{aligned}$$

b.

$$\Delta G^\circ = -RT\ln K \quad \Rightarrow \quad K = e^{-\frac{\Delta G^\circ}{RT}}$$

$$\begin{aligned}K &= e^{-\frac{5400\ \text{J/mol}}{(8.314\ \text{J/(mol K)})(325\ \text{K})}} = e^{-2.00} \\ &= 0.135\end{aligned}$$

$$P_{\mathrm{H_2O\,(g)}} = K_p = 0.135\ \text{atm} = 102\ \text{mmHg}$$

At 325 K, $\Delta G^\circ = 5.4\ \text{kJ/mol}$, and the vapour pressure of water is approximately 102 mmHg, which is significantly higher than at 298 K (24 mmHg), showing the effect of temperature.

The identity of the liquid also affects vapour pressure. Stronger intermolecular forces result in lower vapour pressure because

more energy is required for molecules to escape into the gas phase.

In thermodynamic terms, stronger intermolecular forces mean a larger ΔH_{vap}. At a given temperature, this makes ΔG more positive and vaporization less favourable, resulting in a lower equilibrium vapour pressure.

For example, compare the vaporization of diethyl ether and water:

$$\mathrm{CH_3CH_2OCH_2CH_3\,(l)} \rightleftharpoons \mathrm{CH_3CH_2OCH_2CH_3\,(g)}$$

Diethyl ether is a polar molecule that experiences dipole–dipole interactions and dispersion forces, while water forms hydrogen bonds, which are significantly stronger. As a result, diethyl ether has a much higher vapour pressure than water at 298 K:

- Vapour pressure of diethyl ether: 442 mmHg
- Vapour pressure of water: 23.8 mmHg

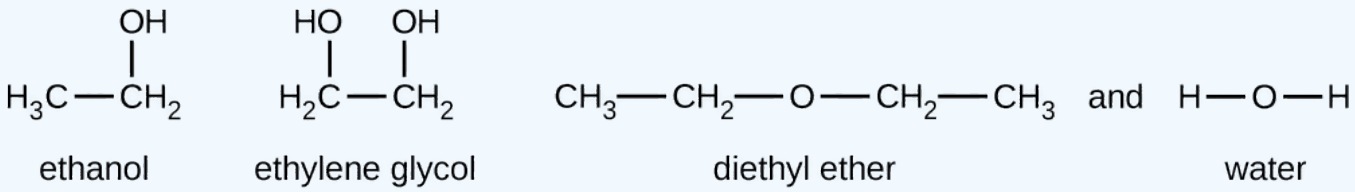
This reflects the difference in enthalpies of vaporization:

- ΔH_{vap} for diethyl ether: 26.0 kJ/mol
- ΔH_{vap} for water: 44.0 kJ/mol

These values illustrate that weaker intermolecular forces lead to lower enthalpies of vaporization and higher vapour pressures, while stronger intermolecular forces do the opposite.

Example 10.7.3: Explaining Vapour Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapour pressures in terms of types and extents of IMFs:



Solution

The vapour pressure of a substance depends on the strength of its intermolecular forces (IMFs): stronger IMFs mean fewer molecules escape to the gas phase, resulting in lower vapour pressure.

- Diethyl ether has London dispersion and dipole–dipole forces but cannot hydrogen bond. It has the weakest IMFs and the highest vapour pressure.
- Ethanol can form hydrogen bonds due to its $-\mathrm{OH}$ group. Its IMFs are stronger than those of diethyl ether, so it has a lower vapour pressure.
- Water forms extensive hydrogen bonds and has stronger IMFs than ethanol. Its vapour pressure is lower than that of ethanol.
- Ethylene glycol has two $-\mathrm{OH}$ groups and can form even more hydrogen bonds. Its strongest overall IMFs give it the lowest vapour pressure of the four.

Figure 10.7.5 shows how temperature and intermolecular forces affect the vapour pressure of different substances. For each liquid, vapour pressure increases with temperature, but the magnitude depends on the strength of the intermolecular forces. At a given temperature (e.g., 40 °C), we can compare vapour pressures to see the effect of intermolecular forces:

$$\text{water} < \text{ethanol} < \text{diethyl ether}$$

Substances with stronger intermolecular forces have lower vapour pressures at any given temperature.

The boiling point is the temperature at which a liquid's vapour pressure equals the surrounding (external) pressure. At this point,

bubbles of vapour can form inside the liquid and rise to the surface. At lower temperatures, the vapour pressure is too low to push back against atmospheric pressure and boiling cannot occur, although vaporization can occur at the surface. The normal boiling point corresponds to a vapour pressure of 1 atm (101.3 kPa), shown as a dashed line in Figure 10.7.5. Note that the boiling point is highest for water, which has the strongest intermolecular forces and lowest for diethyl ether with the weakest intermolecular forces.

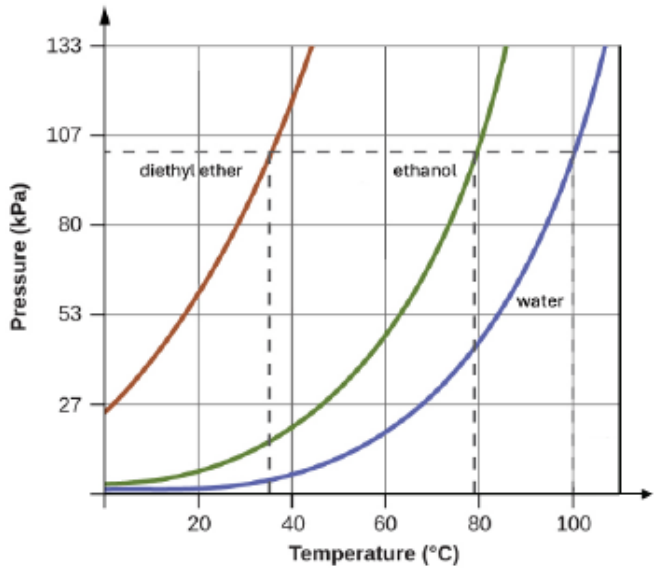


Figure 10.7.5: Vapour pressure curves for water, ethanol, and diethyl ether. Vapour pressure increases with temperature for all three substances, but the magnitude depends on the strength of their intermolecular forces. At a given temperature, diethyl ether, with the weakest intermolecular forces, has the highest vapour pressure, while water, with the strongest intermolecular forces, has the lowest vapour pressure. The dashed line indicates 1 atm pressure, which corresponds to the normal boiling point for each substance (the temperature at which its vapour pressure equals atmospheric pressure).

Heating and Cooling Curves

A heating or cooling curve shows how the temperature of a substance changes as it absorbs or releases heat. When no phase change occurs, the relationship between heat (q) and temperature change (ΔT) is given by:

$$q = mc\Delta T$$

where m is the mass of the substance and c is its specific heat capacity.

At the temperature where a phase change occurs (such as melting or boiling), the temperature remains constant even though heat is still being added. During these flat regions (plateaus), the heat goes into overcoming intermolecular forces, not increasing the kinetic energy of the molecules.

Figure 10.7.6 shows a heating curve for water. From –10 °C to 0 °C, heat increases the kinetic energy of water molecules, raising the temperature of the ice. At 0 °C, the melting point, the temperature levels off. Heat energy is now used to disrupt hydrogen bonds, allowing molecules to move past each other and form liquid water. The temperature stays constant until all the ice has melted. The amount of heat requires to completely melt the ice corresponds to the enthalpy of fusion, ΔH_{fus}. From 0 °C to 100 °C, heat again increases molecular kinetic energy, raising the temperature of the liquid. At 100 °C, the boiling point, another plateau appears: heat is now used to fully overcome hydrogen bonding so that molecules can separate into the gas phase. The amount of heat needed for the water to completely boil corresponds to the enthalpy of vaporization, ΔH_{vap}. The plateau at 100 °C is longer than at 0 °C because vaporization requires more energy than fusion. Vaporization involves a much larger separation of molecules, so $\Delta H_{\text{vap}} > \Delta H_{\text{fus}}$. Once all the water has vaporized, any additional heat increases the kinetic energy and temperature of the water vapour.

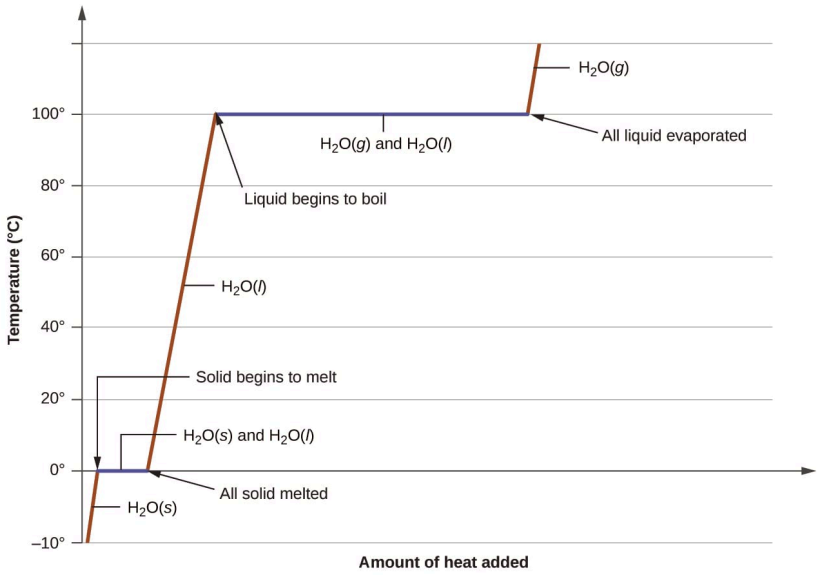


Figure 10.7.6: A heating curve for water showing how temperature changes as heat is added. The flat portions of the curve represent phase changes (melting at 0 °C and boiling at 100 °C) where the added heat is used to overcome intermolecular forces rather than increase temperature.

Phase Diagrams

In earlier sections, we explored how temperature affects phase changes. In this section, we examine how both temperature and pressure influence the physical state of a substance, using phase diagrams.

A phase diagram shows the most stable physical states (solid, liquid, or vapour) of a pure substance under different combinations of temperature and pressure. Each region in the diagram represents the conditions under which a particular phase is the most stable. A typical phase diagram is shown in (Figure 10.7.7).

Each region corresponds to the range of combinations of temperature and pressure over which that phase is the most stable:

- The solid region appears at low temperature and high pressure (upper left).
- The vapour region appears at high temperature and low pressure (lower right).
- The liquid region lies between them.
- At very high temperatures and pressures (upper right), the substance becomes a supercritical fluid, a phase that has properties of both gases and liquids.

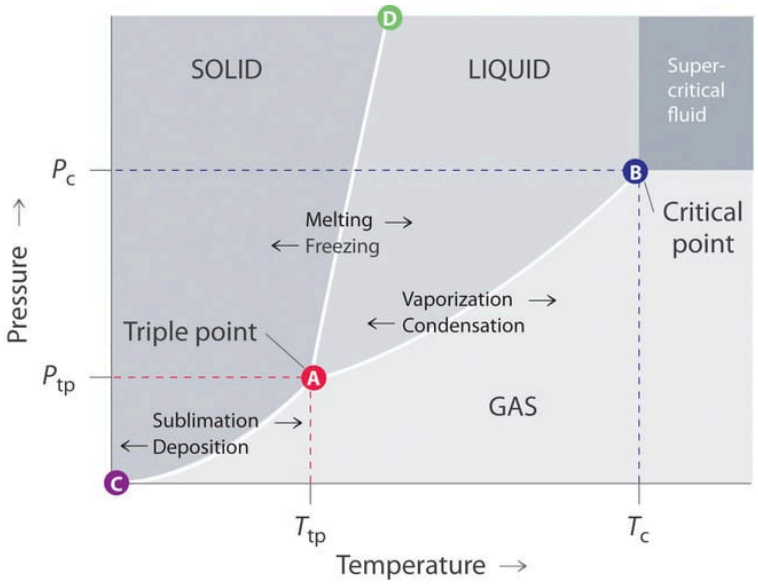


Figure 10.7.7: A typical phase diagram showing the three common phases (solid, liquid, gas) and a supercritical region. Lines represent phase boundaries where two phases coexist in equilibrium.

The lines in a phase diagram represent the combinations of temperature and pressure at which two phases coexist in equilibrium:

- Solid–liquid line (A to D): Shows how the melting point changes with pressure. Moving across this line corresponds to melting or freezing.
- Liquid–vapour line (A to B): This is the liquid vapour pressure curve. It shows the pressure at which liquid and gas are in equilibrium at different temperatures. It ends at the critical point, beyond which the liquid and vapour phases merge into a supercritical fluid. Moving across this line corresponds to vaporization or condensation.
- Solid–vapour line (A to C): This is the solid vapour pressure curve (or sublimation curve). It shows the pressure at which solid and gas are in equilibrium at different temperatures. Moving across this line corresponds to sublimation (solid → gas) or deposition (gas → solid).

Point A, where all three lines meet, is the triple point. This is the only combination of temperature and pressure where all three phases (solid, liquid, and vapour) coexist in equilibrium. A pure substance can only have one triple point.

Point B is the critical point. As temperature increases in a closed container, the molecules in the liquid phase become increasingly far apart, decreasing the density of the liquid. At the same time, as the liquid continues to evaporate, the gas phase becomes increasingly dense, and the distance between gas molecules decreases. Above a certain critical temperature (T_c) and critical pressure (P_c), the liquid and gas phases become equal in density and the boundary between the two phases disappears, forming one homogenous phase, a supercritical fluid, with the properties of both gases and liquids. Supercritical fluids can diffuse like gases but dissolve materials like liquids.

Keep in mind that a phase diagram like this applies to a single pure substance in a closed system. While most lab experiments are done in open containers, the general conclusions from phase diagrams still apply in many cases.

The reason why temperature and pressure influence the physical state of a substance relates to the fact that ΔG is dependent on both temperature and pressure. As temperature and pressure are varied, the ΔG value of the solid, liquid, and gas states of a substance also changes. The most stable phase at a certain temperature and pressure is the phase with the lowest ΔG at those conditions. When two phases have equal ΔG values at a certain temperature and pressure, they are at equilibrium.

We have examined in this chapter the temperature dependence of ΔG. The pressure dependence of ΔG is covered in second-year thermodynamics courses.

The Phase Diagram of Water

Let's now examine the phase diagram of a specific substance: water (Figure 10.7.8).

The triple point of water occurs at 0.0098 °C and 0.0060 atm. This is the lowest pressure at which liquid water can exist. Below this pressure, ice doesn't melt as it warms. Instead, it sublimes directly into water vapour. This principle is the basis for freeze-drying: foods or beverages are frozen and then placed under very low pressure (below 0.0060 atm). As the sample is gently warmed, the ice sublimes, removing water without passing through the liquid phase. This allows for preservation without altering texture or taste.

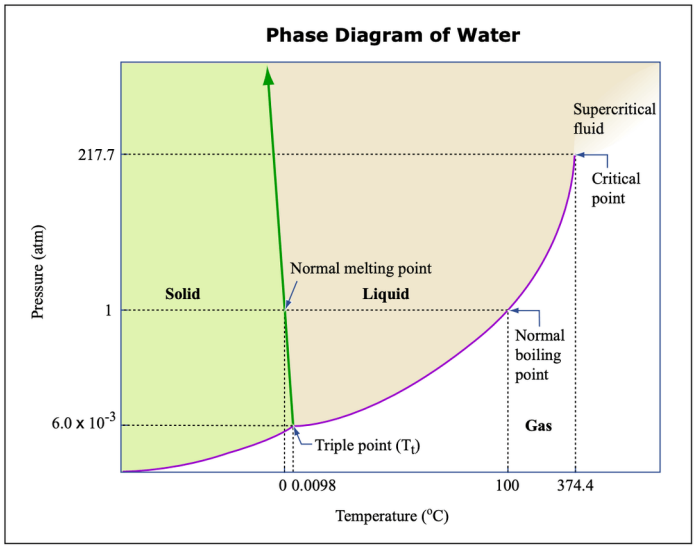


Image by MIT OpenCourseWare.

Figure 10.7.8: Phase diagram of water. Note the negative slope of the solid–liquid boundary, which means that increasing pressure can melt ice. The triple point (0.01 °C, 0.006 atm) is the only temperature and pressure at which all three phases coexist in equilibrium. Note: Axes are not drawn to scale. (CC BY-SA 3.0; Wikimedia Commons)

A unique feature of water's phase diagram is the negative slope of the solid–liquid boundary. Most substances melt at higher temperatures under higher pressures, but ice melts at lower temperatures as pressure increases. This unusual behaviour occurs because ice is less dense than liquid water — applying pressure pushes the molecules closer together, favouring the denser liquid phase.

This property is environmentally critical. If ice were denser than water, it would sink, lakes would freeze from the bottom up, and aquatic ecosystems would be unable to survive winter. The negative slope of the melting curve explains why ice floats and why water expands upon freezing.

Example 10.7.4: Water

Referring to the phase diagram of water in Figure 10.7.8:

a. What is the physical state of water at 400°C and 150 atm?
b. What phase changes occur as the sample is slowly cooled from 400°C to -50°C at a constant pressure (150 atm)?

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

a. Locate the initial conditions on the phase diagram to identify the phase present.

b. Follow a horizontal line (constant pressure) from high to low temperature to track the phase changes.

Solution:

a. At 400 °C and 150 atm (Figure 10.7.8), the sample lies in the gas region, so the water is in the form of water vapour.

b. As the sample cools at constant pressure (150 atm), we move horizontally left on the phase diagram:

- The line first crosses the liquid–vapour boundary, so condensation begins. The sample becomes a mixture of vapour and liquid.
- Once all vapour has condensed, the sample enters the liquid region and is now entirely liquid.
- As cooling continues, the line crosses the melting curve. Freezing begins, and the sample becomes a mixture of ice and water.
- After all water has frozen, further cooling brings the sample into the solid region: the final state is ice at –50 °C and 150 atm.

Exercise 10.7.2

Referring to the phase diagram of water in Figure 10.7.8, predict the physical form of a sample of water at 0 °C as the pressure is gradually increased from 0.0050 atm to 250 atm.

Answer available at the end of this section.

The Phase Diagram of Carbon Dioxide

In contrast to water, carbon dioxide has a more typical phase diagram, with a melting curve that slopes upward to the right (Figure 10.7.10). The triple point for $\mathrm{CO_2\,(s)}$ is at -56.6 °C and 5.11 atm, which means that liquid $\mathrm{CO_2\,(s)}$ cannot exist below at pressures below 5.11 atm.

At 1 atm, for example, $\mathrm{CO_2\,(s)}$ does not melt when heated. Instead, it sublimes directly from solid to gas at –78.5 °C. This is why solid $\mathrm{CO_2\,(s)}$ is called dry ice: it turns into vapour without forming a liquid at room temperature (Figure 10.7.9).



Figure 10.7.9: Dry ice ($\mathrm{CO_2\,(s)}$) subliming in air at room temperature and pressure. (Image: Wikipedia, CC BY-SA)

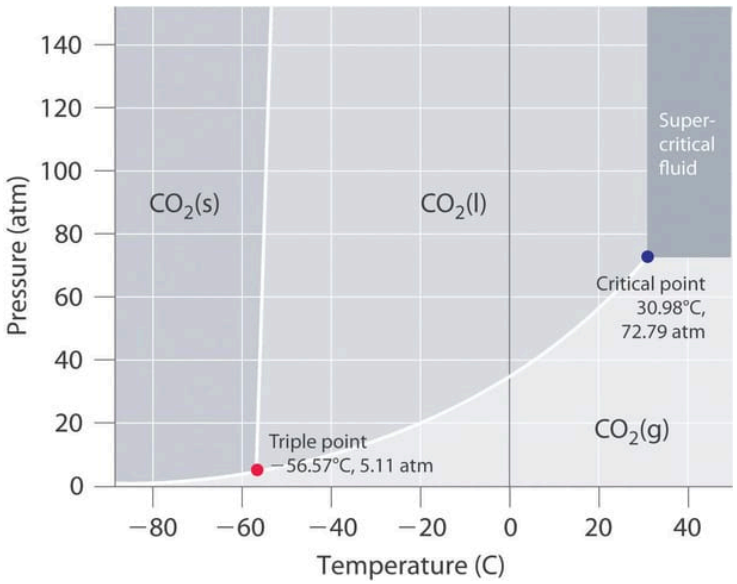


Figure 10.7.10: The phase diagram of carbon dioxide. Note the triple point (–56.6 °C, 5.11 atm), the critical point (30.98 °C, 72.79 atm), and the normal sublimation temperature (–78.5 °C at 1 atm).

The critical point for carbon dioxide is at 30.98 °C and 72.79 atm. Above these conditions, CO_2 exists as a supercritical fluid, a phase with properties of both gases and liquids. Supercritical carbon dioxide is used in green technologies, including as a refrigerant, in coffee decaffeination, and in natural product extraction. Its relatively low critical temperature and environmental safety make it an attractive option for heat pumps and low-carbon cooling systems.

Exercise 10.7.3

Referring to the phase diagram of carbon dioxide in Figure 10.7.10, predict the physical form of a sample of carbon dioxide at -60 °C as the pressure is gradually increased from 0.1 atm to 60 atm.

Answer available at the end of this section.

Chemistry in Everyday Life: Decaffeinating Coffee Using Supercritical CO_2

Coffee contains hundreds of compounds that contribute to its flavour and aroma, and one that keeps us awake: caffeine. For people who enjoy coffee but want to avoid caffeine, decaffeinated coffee is a popular option.

Traditional methods for removing caffeine often use water or organic solvents like dichloromethane or ethyl acetate, which can also extract flavour compounds and may leave behind traces of solvent.

A more effective and environmentally friendly approach uses supercritical carbon dioxide (CO_2). At temperatures above 31 °C and pressures above 73 atm, CO_2 becomes a supercritical fluid with properties of both gases and liquids. Like a gas, it can penetrate deep into coffee beans; like a liquid, it can dissolve caffeine effectively.

In this process (Figure 10.7.11), steamed coffee beans are treated with supercritical CO_2, which removes 97–99% of the caffeine while preserving flavour and aroma. After extraction, the CO_2 is depressurized and easily removed, leaving behind decaffeinated beans and recoverable caffeine for other uses.

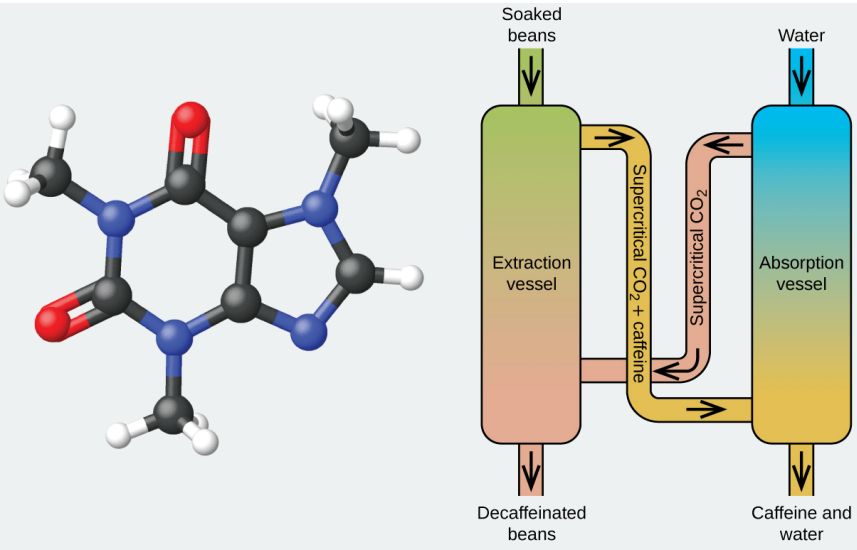


Figure 10.7.11: (a) Caffeine's structure makes it soluble in both polar and nonpolar solvents. (b) Supercritical CO_2 extraction removes caffeine without affecting taste.

Summary

- Phase transitions are changes between solid, liquid, and gas phases. These include melting, freezing, vaporization, condensation, sublimation, and deposition.
- Phase changes involve changes in both enthalpy (ΔH) and entropy (ΔS).
  - Transitions that move particles farther apart (e.g., melting, vaporization, sublimation) require heat to overcome intermolecular forces ($\Delta H > 0$) and increase entropy ($\Delta S > 0$).
  - Transitions that bring particles closer together (e.g., condensation, freezing, deposition) release heat ($\Delta H < 0$) and decrease entropy ($\Delta S < 0$).
- The Gibbs free energy change ($\Delta G = \Delta H - T\Delta S$) determines whether a phase change is spontaneous at a given temperature.
  - For processes with $\Delta H > 0$ and $\Delta S > 0$, such as vaporization, spontaneity increases with temperature.
  - For processes with $\Delta H < 0$ and $\Delta S < 0$, such as freezing, spontaneity increases with a decrease in temperature.
- Vapour pressure is the pressure exerted by the gas phase of a substance in equilibrium with its liquid or solid. It increases with temperature and is higher for substances with weaker intermolecular forces.
- The boiling point is the temperature at which the vapour pressure of the liquid equals the external pressure. The normal boiling point is the temperature at which the vapour pressure is 1 atm.
- Heating and cooling curves show how temperature changes as heat is added or removed. Temperature remains constant during phase changes, as heat goes into overcoming intermolecular forces.
- Phase diagrams show the stable phase of a substance at different temperatures and pressures. They include regions for solid, liquid, and gas, and show phase boundaries where two phases coexist in equilibrium.
- The triple point is the unique combination of temperature and pressure at which all three phases coexist. The critical point marks the end of the liquid–vapour boundary; above this temperature and pressure, the substance exists as a supercritical fluid.

Glossary

boiling point
: The temperature at which the vapor pressure of a liquid equals the pressure of the gas above it.

critical point
: The temperature and pressure above which a gas cannot be condensed into a liquid.

deposition
: Change from a gaseous state directly to a solid state.

freezing
Change from a liquid state to a solid state.

heating/cooling curve
A graph illustrating how the temperature of a substance changes as it absorbs or releases heat.

melting
Change from a solid state to a liquid state.

melting point
The temperature at which the solid and liquid phases of a substance are in equilibrium.

normal boiling point
The temperature at which a liquid's vapor pressure equals 1 atm (760 torr).

phase change
When a substance transitions between solid, liquid, and gas phases; also called phase transition.

phase diagram
A pressure-temperature graph summarizing conditions under which the phases of a substance can exist.

sublimation
Change from solid state directly to gaseous state.

supercritical fluid
A substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states.

triple point
The temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium.

vapor pressure
The pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature.

vaporization
Change from liquid state to gaseous state.

Answers

Exercise 10.7.1

a. $$\Delta H^\circ_{\text{sub}} = \Delta H^\circ_f(\text{I}_2\,(\text{g})) - \Delta H^\circ_f(\text{I}_2\,(\text{s})) = 64.4\ \text{kJ/mol} - (0\ \text{kJ/mol}) = 64.4\ \text{kJ/mol}$$

b. $$\Delta S^\circ_{\text{sub}} = S^\circ(\text{I}_2\,(\text{g})) - S^\circ(\text{I}_2\,(\text{s})) = 260.7\ \text{J/mol·K} - 116.1\ \text{J/mol·K} = 144.6\ \text{J/mol·K}$$

c. $$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 64.4\ \text{kJ/mol} - (298\ \text{K})(144.6\ \text{J/mol·K})\left(\frac{\text{kJ}}{1000\ \text{J}}\right) = 21.3\ \text{kJ/mol}$$

Since $\Delta G^\circ > 0$, sublimation is not spontaneous under standard state conditions at 298 K.

d. To find the temperature where $\Delta G^\circ = 0$, solve:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{64.4\ \text{kJ/mol}}{144.6;\text{J/mol·K}} \cdot \left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right) = 445\ \text{K}$$

This is the sublimation point of I_2 under standard pressure.

Exercise 10.7.2

At 0 °C and 0.0050 atm, the sample is in the gas region (water vapour).

As pressure increases:

- The line crosses the sublimation curve, and the vapour undergoes deposition to form solid ice.
- With continued pressure increase, the line crosses the melting curve (at around 1 atm), and the ice undergoes melting, forming liquid water.

Exercise 10.7.3

At -60 °C and 0.1 atm, the sample is in the gas region (CO_2 vapour). As pressure increases, the line crosses the sublimation curve, and the vapour undergoes deposition, forming solid CO_2 (dry ice). As pressure increases further, the sample remains in the solid region. Solid CO_2 does not melt at this temperature, since −60 °C is below the triple point.

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10.E: Thermodynamics (Exercises)

Spontaneity

Exercise $10.E.1$*

What is a spontaneous reaction?

Answer available at the end of this section.

Exercise $10.E.2$*

Indicate whether the following processes are spontaneous or nonspontaneous.

a. Liquid water freezing below 0°C (the freezing point of water)
b. Liquid water freezing above 0°C (the freezing point of water)
c. A ball thrown upward into the air
d. A raindrop falling to the ground
e. Iron rusting when exposed to air and moisture

Answer available at the end of this section.

Exercise $10.E.3$**

Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

Answer available at the end of this section.

Exercise $10.E.4$*

When you add a sugar cube to hot coffee, it dissolves and disperses in the coffee.

a. Is this process spontaneous?
b. Is the reverse process, the sugar crystallizing, spontaneous or nonspontaneous?

Answer available at the end of this section.

Exercise $10.E.5$*

Can a nonspontaneous process occur?

Answer available at the end of this section.

Entropy

Exercise $10.E.6$*

At room temperature, iodine (I_2) is a solid, bromine (Br_2) is a liquid, and chlorine (Cl_2) is a gas. Place the three halogens in order of increasing entropy.

Answer available at the end of this section.

Exercise $10.E.7$*

For each pair, indicate which substance has the higher entropy. Briefly explain your reasoning.

a. $C_2H_5OH\,(l)$ or $C_3H_7OH\,(l)$
b. $C_2H_5OH\,(l)$ or $C_2H_5OH\,(g)$
c. 2 moles of $H_2\,(g)$ or 1 mole of $H_2\,(g)$
d. $N_2H_4\,(g)$ or $N_2\,(g)$
e. $H_2\,(g)$ or $Na_2CO_3\,(s)$

Answer available at the end of this section.

Exercise $10.E.8$*

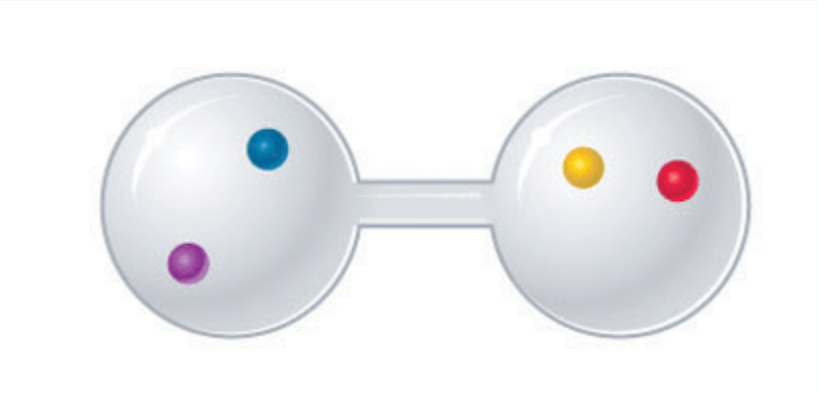
Predict the sign of the entropy change (ΔS) for each of the following processes. Give a reason for your prediction.

a. $Pb^{2+}\,(aq) + S^{2-}\,(aq) \rightarrow PbS\,(s)$
b. $4\,Fe\,(s) + 3\,O_2\,(g) \rightarrow 2\,Fe_2O_3\,(s)$
c. $2\,C_6H_{14}\,(l) + 19\,O_2\,(g) \rightarrow 14\,H_2O\,(g) + 12\,CO_2\,(g)$
d. $Ca\,(s) + 2\,H_2O\,(l) \rightarrow Ca(OH)_2\,(aq) + H_2\,(g)$
e. $C_2H_2\,(g) + 2\,H_2\,(g) \rightarrow C_2H_6\,(g)$
f. $2\,HCl\,(aq) + K_2CO_3\,(aq) \rightarrow 2\,KCl\,(aq) + H_2O\,(l) + CO_2\,(g)$

Answer available at the end of this section.

Exercise $10.E.9$**

In the example of four gas molecules in a two-bulb container, the most probable arrangement is two molecules in each bulb.



a. Why is this arrangement more probable than having all four molecules in one bulb?

b. How is this related to the concept of entropy?

Answer available at the end of this section.

The Second and Third Law of Thermodynamics

Exercise $10.E.10$*

Consider the following reaction:

$$2\,\mathrm{CO\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{CO_2\,(g)} \qquad \Delta\mathrm{H} = -566\,\mathrm{kJ/mol}$$

a. What is the sign of ΔS for the reaction?

b. Is there any temperature at which this reaction could be spontaneous? Explain.

Answer available at the end of this section.

Exercise $10.E.11$*

What is the sign of ΔS_{surr} for:

a. an endothermic reaction?
b. an exothermic reaction?

Answer available at the end of this section.

Exercise $10.E.12$*

According to the Third Law of Thermodynamics, the entropy of a perfect crystal is zero at 0 K. What does this imply about the motion and arrangement of particles in a perfect crystal at absolute zero?

Answer available at the end of this section.

Exercise $10.E.13$*

Predict the sign of ΔS° for each process. Then calculate ΔS° at 298 K, using the values for the standard molar entropies in the reference table.

Reactions:

a. $\mathrm{CS_2\,(g)} \rightarrow \mathrm{CS_2\,(l)}$
b. $\mathrm{Cu\,(s)} \rightarrow \mathrm{Cu\,(g)}$
c. $2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \rightarrow 2\,\mathrm{H_2O\,(l)}$
d. $2\,\mathrm{S\,(s)} + 3\,\mathrm{O_2\,(g)} \rightarrow 2\,\mathrm{SO_3\,(g)}$
e. $\mathrm{SO_3\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \mathrm{H_2SO_4\,(aq)}$
f. $\mathrm{NH_4NO_3\,(s)} \rightarrow \mathrm{N_2O\,(g)} + 2\,\mathrm{H_2O\,(g)}$

Answer available at the end of this section.

Free Energy

Exercise $10.E.14$*

Calculate the standard free energy change at 298 K using the values for the standard free energies of formation in the reference table. Are the reactions spontaneous under standard state conditions?

a. $\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$
b. $\mathrm{H_2\,(g) + Br_2\,(l) \rightleftharpoons 2\,HBr\,(g)}$
c. $\mathrm{MnO_2\,(s) \rightleftharpoons Mn\,(s) + O_2\,(g)}$

Answer available at the end of this section.

Exercise $10.E.15$**

Consider the following reaction:

$\mathrm{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)}$

What is the standard free energy change (ΔG°) at

(a) 298 K

(b) 1225 K?

Thermodynamic data at 298 K:

	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/(mol · K))
$\mathrm{CaCO_3\,(s)}$	-1207.6	-1129.1	91.7
$\mathrm{CaO\,(s)}$	-634.9	-603.3	38.1
$\mathrm{CO_2\,(g)}$	-393.5	-394.4	213.8

Assume ΔH° and ΔS° do not change significantly with temperature.

(c) Why is the reaction spontaneous at higher temperatures?

Answer available at the end of this section.

Exercise $10.E.16$**

For the previous reaction in Exercise $10.E.15$, at what temperature will the reaction switch from being nonspontaneous to spontaneous under standard state conditions? Use the data from the previous question.

Answer available at the end of this section.

Exercise $10.E.17$**

Consider the following reaction:

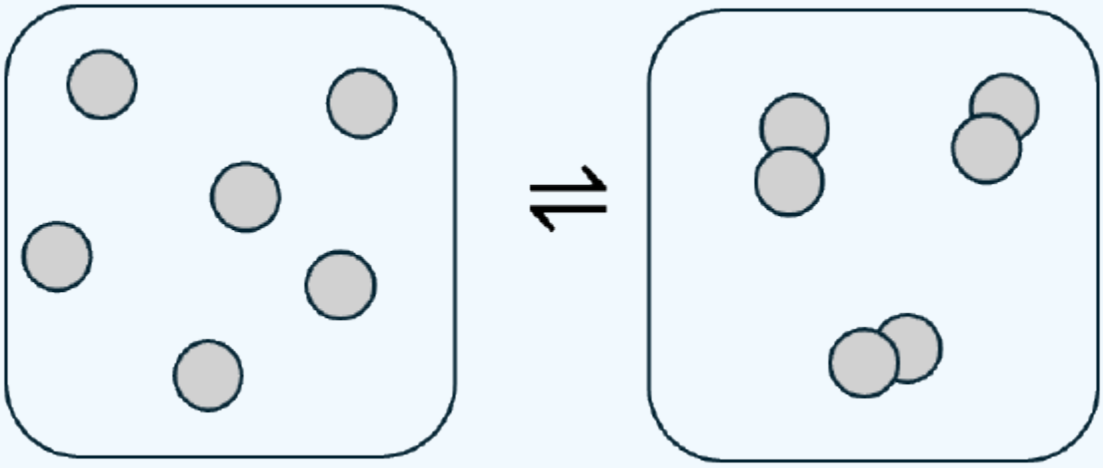
$\mathrm{CaO\,(s) + 3\,C\,(s) \rightleftharpoons CaC_2\,(s) + CO\,(g)} \quad \Delta H^\circ = 464.6\ \mathrm{kJ/mol}$

Is the reaction spontaneous at all temperatures, only at lower temperatures, only at higher temperatures, or nonspontaneous at all temperatures? Explain your reasoning.

Answer available at the end of this section.

Exercise $10.E.18$***

Consider the following molecular scene:



(a) Predict the sign of ΔS° and ΔH°.

(b) Is the reaction spontaneous at all temperatures, only at lower temperatures, only at higher temperatures, or nonspontaneous at all temperatures? Explain your reasoning.

Answer available at the end of this section.

Exercise $10.E.19$**

Consider the following reaction:

$$2\,\mathrm{Na\,(s)} + 2\,\mathrm{H_2O\,(l)} \rightleftharpoons 2\,\mathrm{NaOH\,(aq)} + \mathrm{H_2\,(g)} \quad \Delta H^\circ = -368.4\ \mathrm{kJ/mol}$$

Is the reaction spontaneous at all temperatures, only at lower temperatures, only at higher temperatures, or nonspontaneous at all temperatures? Explain your reasoning.

Answer available at the end of this section.

Exercise $10.E.20$**

For the following reaction:

$$2\,\mathrm{Al\,(s)} + 3\,\mathrm{Cl_2\,(g)} \rightleftharpoons 2\,\mathrm{AlCl_3\,(s)}$$

(a) What is the standard free energy change (ΔG°) at 25 °C?

(b) At what temperature will the reaction switch from being spontaneous to nonspontaneous under standard state conditions?

Thermodynamic data at 298 K:

	ΔH_f° (kJ/mol)	S° (J/(mol · K))
$\mathrm{Al(s)}$	0	28.3
$\mathrm{Cl_2(g)}$	0	223.1
$\mathrm{AlCl_3(s)}$	-704.2	109.3

Assume ΔH° and ΔS° do not change significantly with temperature.

Answer available at the end of this section.

Exercise $10.E.21$**

Two chemical reactions are shown below:

1. Conversion of methane to ethane and hydrogen:

$$2\,\mathrm{CH_4(g)} \longrightarrow \mathrm{C_2H_6(g)} + \mathrm{H_2(g)} \quad \Delta G^\circ = +68.1\ \mathrm{kJ/mol}$$

2. Formation of water:

$$\mathrm{H_2(g)} + \frac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{H_2O(g)} \quad \Delta G^\circ = -228.6\ \mathrm{kJ/mol}$$

(a) Write the overall chemical equation that results from coupling these two processes to give the reaction of methane with oxygen gas.

(b) Calculate the overall standard free energy change, ΔG°, for the coupled process.

(c) Is the overall coupled reaction spontaneous under standard conditions? Explain.

Answer available at the end of this section.

Exercise $10.E.22$**

A reaction has $\Delta H^\circ_{298} = 100\ \mathrm{kJ/mol}$ and $\Delta S^\circ_{298} = 250\ \mathrm{J/mol{\cdot}K}$.

(a) Is the reaction spontaneous at room temperature under standard state conditions?

(b) If not, under what temperature conditions will it become spontaneous? (Assume ΔH° and ΔS° do not change significantly with temperature.)

(c) What is the standard free energy change (ΔG°) at 650 K?

Answer available at the end of this section.

Free Energy, Equilibrium, and Non-Standard State Conditions

Exercise $10.E.23$**

If $\Delta G^\circ < 0$ at 298 K, is the reaction always spontaneous at 298 K?

Answer available at the end of this section.

Exercise $10.E.24$**

What is the relationship between Q and K and the sign of ΔG when:
(a) the reaction is spontaneous in the forward direction?
(b) the reaction is at equilibrium?
(c) the reaction is nonspontaneous in the forward direction?

Answer available at the end of this section.

Exercise $10.E.25$**

Why might a reaction with a very large K not proceed spontaneously?

Answer available at the end of this section.

Exercise $10.E.26$*

For the following reaction at 298 K:

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g) \quad \Delta G^\circ = -457.18\,kJ/mol$$

what is ΔG at 298 K when P_{H_2} = 2.0 atm; P_{O_2} = 2.0 atm; P_{H_2O} = 0.010 atm?

Answer available at the end of this section.

Exercise $10.E.27$*

For the following reaction at 298 K:

$$2\,LiOH\,(s) + CO_2\,(g) \longrightarrow Li_2CO_3\,(s) + H_2O\,(g) \quad \Delta G^\circ = -79\,kJ/mol$$

what is ΔG at 298 K?

(a) when P_{CO_2} = 2.0 atm; P_{H_2O} = 0.10 atm; with excess $LiOH\,(s)$ and $Li_2CO_3\,(s)$ present?

(b) when P_{CO_2} = 0.00010 atm; P_{H_2O} = 2.0 atm; with excess $LiOH\,(s)$ and $Li_2CO_3\,(s)$ present?

Answer available at the end of this section.

Exercise $10.E.28$*

Calculate the equilibrium constant at 25 °C for each of the following reactions:

(a) $O_2\,(g) + 2\,F_2\,(g) \longrightarrow 2\,OF_2\,(g) \quad \Delta G^\circ = -9.2\,kJ/mol$

(b) $I_2\,(s) + Br_2\,(l) \longrightarrow 2\,IBr\,(g) \quad \Delta G^\circ = 7.3\,kJ/mol$

(c) $2\,LiOH\,(s) + CO_2\,(g) \longrightarrow Li_2CO_3\,(s) + H_2O\,(g) \quad \Delta G^\circ = -79\,kJ/mol$

Answer available at the end of this section.

Exercise $10.E.29$**

Calculate K_p for the following reaction at 298 K using the provided thermodynamic data:

$\mathrm{Fe_2O_3\,(s) + 3\,CO\,(g) \longrightarrow 2\,Fe\,(s) + 3\,CO_2\,(g)}$

Thermodynamic data at 298 K:

	$\Delta H_f^\circ (\mathrm{kJ/mol})$	$S^\circ (\mathrm{J/(mol \cdot K)})$
$\mathrm{Fe_2O_3\,(s)}$	-842.2	87.4
$\mathrm{CO\,(g)}$	-110.5	197.7
$\mathrm{Fe\,(s)}$	0	27.3
$\mathrm{CO_2\,(g)}$	-393.5	213.8

Answer available at the end of this section.

Exercise $10.E.30$*

Calculate ΔG° for each of the following reactions from the equilibrium constant at the temperature given.

(a) $\mathrm{N_2\,(g) + O_2\,(g) \longrightarrow 2\,NO\,(g)}$ $\quad \mathrm{T = 2000\ ^\circ C}$ $\quad K_p = 4.1 \times 10^{-4}$

(b) $\mathrm{H_2\,(g) + I_2\,(g) \longrightarrow 2\,HI\,(g)}$ $\quad \mathrm{T = 400\ ^\circ C}$ $\quad K_p = 50.0$

(c) $\mathrm{CO_2\,(g) + H_2\,(g) \longrightarrow CO\,(g) + H_2O\,(g)}$ $\quad \mathrm{T = 980\ ^\circ C}$ $\quad K_p = 1.67$

(d) $\mathrm{AgBr\,(s) \longrightarrow Ag^+\,(aq) + Br^-\,(aq)}$ $\quad \mathrm{T = 25\ ^\circ C}$ $\quad K_p = 3.3 \times 10^{-13}$

Answer available at the end of this section.

Exercise $10.E.31$***

Consider the following reaction:

$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2\,(g)}$

At 298 K, ΔH° = 179.2 kJ/mol and ΔS° = 160.2 J/(mol K).

(a) Does the spontaneity of the reaction under standard state conditions change with temperature?

(b) What is ΔG° at 1225 K, assuming ΔH° and ΔS° do not change significantly with temperature?

(c) Given this value of ΔG°, is K = 1, K > 1, K < 1 at 1225 K?

(d) What is the value of K at 1225 K?

(e) The reaction takes place in a closed system containing only solid $\mathrm{CaCO_3}$ and CaO at equilibrium. What is the equilibrium pressure of $\mathrm{CO_2}$ at 1225 K?

Answer available at the end of this section.

Phase Transitions and Phase Diagrams

Exercise $10.E.32$*

What are the signs of ΔH, ΔS, and ΔG for the spontaneous melting of a solid?

Answer available at the end of this section.

Exercise $10.E.33$**

Consider the melting of sodium chloride:

$$\mathrm{NaCl(s)} \rightleftharpoons \mathrm{NaCl(l)} \quad \Delta H^\circ_{\text{fusion}} = 28.16\ \text{kJ/mol} \quad \Delta S^\circ_{\text{fusion}} = 26.22\ \text{J/(mol·K)}$$

Assuming ΔH° and ΔS° do not change with temperature:

(a) Is melting spontaneous at 575 K?

(b) Calculate the melting point of $\mathrm{NaCl(s)}$.

Answer available at the end of this section.

Exercise $10.E.34$**

Find the normal boiling point of $\mathrm{Br_2}$ using the thermodyamic data below:

$$\mathrm{Br_2(l)} \rightleftharpoons \mathrm{Br_2(g)}$$

Assume ΔH° and ΔS° do not change with temperature.

Thermodynamic data at 298 K:

	ΔH°_f (kJ/mol)	S° (J/(mol · K))
$\mathrm{Br_2(l)}$	0	152.2
$\mathrm{Br_2(g)}$	30.9	245.5

Answer available at the end of this section.

Exercise $10.E.35$*

What is the relationship between vapour pressure and temperature? Explain your answer.

Answer available at the end of this section.

Exercise $10.E.36$**

Which substance has the greater vapour pressure at 273 K:

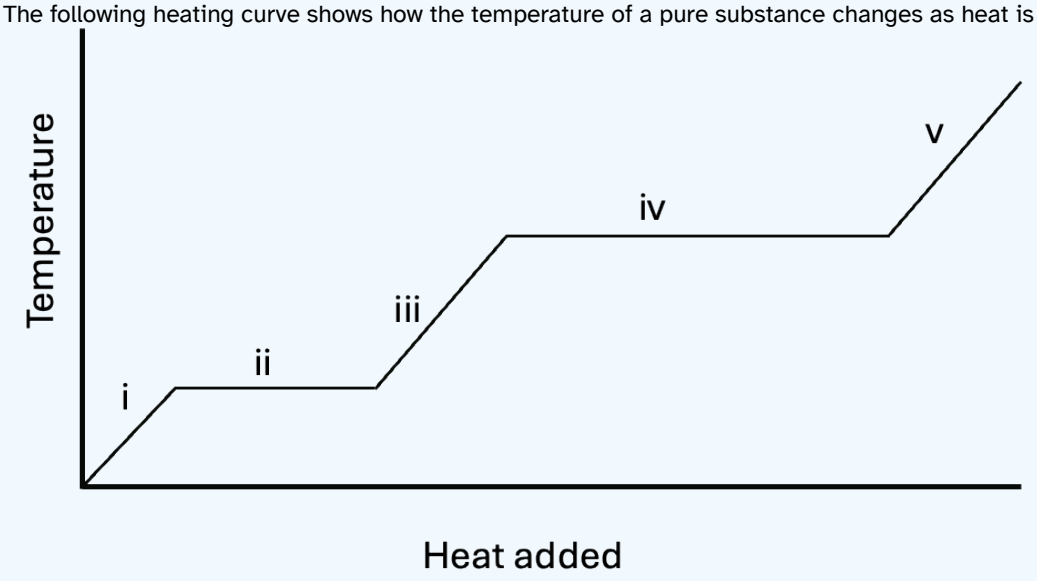
(a) $\mathrm{NH_3}$ or $\mathrm{PH_3}$

(b) $\mathrm{CH_3CH_2OH}$ or $\mathrm{CH_3CH_2Cl}$

Answer available at the end of this section.

Exercise $10.E.37$*

The following heating curve shows how the temperature of a pure substance changes as heat is added at a constant rate:



1. Identify which segment corresponds to:

(a) the solid being heated

(b) the liquid being heated

(c) the gas being heated

(d) melting

(e) boiling

2. Why does the temperature stay constant during the melting and boiling processes?

Answer available at the end of this section.

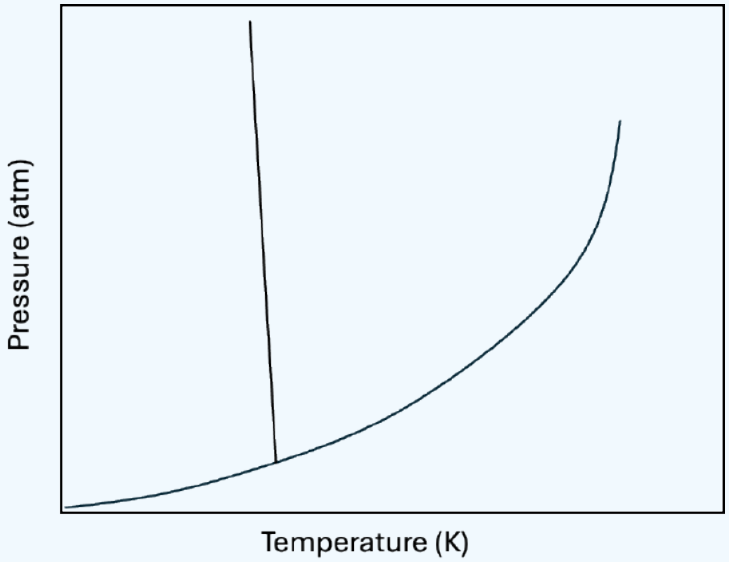
Exercise $10.E.38$**

Krypton is an inert gas used in lighting. It has normal boiling and freezing points of 120.9 K and 116.6 K, respectively. The triple point of krypton is 104.2 K at 0.18 atm. Use these data to sketch a phase diagram for krypton and label all the regions. (The diagram does not need to be to scale.) Is solid krypton more or less dense than liquid krypton?

Answer available at the end of this section.

Exercise $10.E.39$*

Use the unlabeled phase diagram for water to answer the following questions:



Triple point: 0.01 °C, 0.006 atm

Critical point: 374.4 °C, 217.7 atm

Normal melting point: 0 °C, Normal boiling point: 100 °C

(a) What is the maximum pressure at which ice and water vapour can coexist in equilibrium?

(b) What happens to a sample of water at 50 °C and 0.006 atm when the pressure is increased to 10 atm at 50 °C?

(c) Describe the phase changes that occur as a sample at 200 °C and 1.0 atm is cooled at constant pressure to –10 °C.

Answer available at the end of this section.

Additional Problems

Exercise $10.E.40$***

What is the difference between ΔG, ΔG°, and ΔG° at 500 K for a chemical reaction?

Answer available at the end of this section.

Exercise $10.E.41$**

Why is $\Delta H_{\text{vap}} > \Delta H_{\text{fus}}$ for a substance?

Answer available at the end of this section.

Exercise $10.E.42$***

Determine the standard free energy of formation, $\Delta G_{\mathrm{f}}^{\circ}$, for $\mathrm{S}^{2-}(\mathrm{aq})$, given the following data at 298 K:

- $\Delta G_{\mathrm{f}}^{\circ}(\mathrm{Ag}^{+}(\mathrm{aq})) = +77.1\ \mathrm{kJ/mol}$
- $\Delta G_{\mathrm{f}}^{\circ}(\mathrm{Ag_2S}(\mathrm{s})) = -39.5\ \mathrm{kJ/mol}$
- $K_{\mathrm{sp}}(\mathrm{Ag_2S}) = 8 \times 10^{-51}$

Answer available at the end of this section.

Exercise $10.E.43$***

Determine ΔG° for the decomposition of antimony pentachloride at 448 °C:

$$\mathrm{SbCl_5(g)} \longrightarrow \mathrm{SbCl_3(g)} + \mathrm{Cl_2(g)}$$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.43 g of $\mathrm{SbCl_5}$, 9.14 g of $\mathrm{SbCl_3}$, and 2.84 g of $\mathrm{Cl_2}$.

Answer available at the end of this section.

Exercise $10.E.44$***

When ammonium chloride is added to water and stirred, it dissolves spontaneously, and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

Answer available at the end of this section.

Exercise $10.E.45$***

An important source of copper is the ore chalcocite, a form of copper(I) sulfide. When heated, the $\mathrm{Cu_2S}$ decomposes to form copper and sulfur, as described by the following equation:

$$\mathrm{Cu_2S}(s) \rightleftharpoons 2\,\mathrm{Cu}(s) + \mathrm{S}(s)$$

a. Determine ΔG° for the decomposition of $\mathrm{Cu_2S(s)}$ at 298 K.
b. The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine ΔG° for the process at 298 K.
c. The production of copper from chalcocite is performed by roasting the $\mathrm{Cu_2S}$ in air to produce Cu. By combining the equations from parts (a) and (b), write the equation that describes the roasting of chalcocite, and explain why coupling these reactions makes for a more efficient copper production process.

Thermodynamic data at 298 K:

Substance	ΔG_f° **(kJ/mol)**
$\mathrm{Cu_2S(s)}$	-86.2
$\mathrm{Cu(s)}$	0
$\mathrm{S(s)}$	0
$\mathrm{O_2(g)}$	0
$\mathrm{SO_2(g)}$	-300.1

Answer available at the end of this section.

Answers

Exercise $10.E.1$*****

A spontaneous reaction is one that occurs without the continual input of energy from an external source.

Exercise $10.E.2$*****

a. Spontaneous – Water freezes below its freezing point without added energy.

b. Nonspontaneous – Water does not freeze above its freezing point under normal conditions because freezing requires heat to be removed.

c. Nonspontaneous – The ball requires added energy (a push) to rise; it won't go up on its own.

d. Spontaneous – Gravity causes the raindrop to fall naturally.

e. Spontaneous – Rusting occurs without added energy when iron is exposed to air and moisture.

Exercise $10.E.3$******

Although the oxidation of plastics is thermodynamically spontaneous, the reaction occurs very slowly. Plastics are kinetically stable, meaning the reaction has a high activation energy and proceeds at an extremely slow rate. This means the process is spontaneous but extremely slow, so it doesn't occur noticeably in the environment.

Exercise $10.E.4$*****

a. Yes, the sugar dissolving and dispersing in hot coffee is spontaneous; it occurs without the continual input of energy.

b. The reverse process, sugar crystallizing out of the coffee, is nonspontaneous under these conditions. A process that is spontaneous in one direction is nonspontaneous in the reverse direction unless the conditions change.

Exercise $10.E.5$*****

Yes, but it requires continuous input of energy. For example, water does not flow uphill on its own, but it can be pumped using electricity.

Exercise $10.E.6$*****

$\mathrm{I_2\,(s)} < \mathrm{Br_2\,(l)} < \mathrm{Cl_2\,(g)}$

Entropy is strongly affected by physical state. Gases have the highest entropy, followed by liquids, then solids.

Exercise $10.E.7$*****

a. $\mathrm{C_3H_7OH\,(l)}$ – It is a larger and more complex molecule, so it has more possible motions and microstates, resulting in a higher entropy.

b. $\mathrm{C_2H_5OH\,(g)}$ – Gases have much higher entropy than liquids due to greater freedom of motion and dispersal.

c. 2 moles of $\mathrm{H_2\,(g)}$ – Entropy is an extensive property, so doubling the amount of substance doubles the entropy.

d. $\mathrm{N_2H_4\,(g)}$ - It is a more complex molecule with more atoms and has more internal motions, giving it higher entropy.

e. $\mathrm{H_2\,(g)}$ – Gases have far more freedom of movement and more accessible microstates, so $\mathrm{H_2\,(g)}$ has a greater entropy even though $\mathrm{Na_2CO_3\,(s)}$ is a more complex molecule.

Exercise $10.E.8$*****

a. Negative. A solid precipitate forms from dissolved ions, decreasing the disorder in the system.
b. Negative. Gaseous oxygen is consumed and converted into a solid, resulting in a net decrease in entropy.
c. Positive. The number of gas molecules increases significantly, leading to greater energy dispersal and higher entropy.
d. Positive – A gas is produced from non-gaseous reactants, increasing the dispersal of energy.
e. Negative – The total number of gas molecules decreases from 3 to 1, reducing entropy.
f. Positive – A gas is produced from aqueous reactants, increasing the number of microstates and entropy.

Exercise $10.E.9$******

a. There are more ways (microstates) to arrange the molecules so that two are in each bulb than there are ways for all four molecules to be in one bulb. For example, there is only one microstate where all four molecules are on one side, but there are six different microstates where two molecules are on each side. The arrangement with the most microstates is the most probable.

b. Entropy is a measure of the number of microstates available to a system. Arrangements with more microstates have higher entropy and are more probable. As the molecules spread out into both bulbs, the number of possible microstates increases, so the system's entropy increases. This makes the distribution with two molecules in each bulb more likely than all the molecules being in one bulb.

Exercise $10.E.10$*****

a. $\Delta S_{\text{system}} < 0$. The number of gas molecules decreases from 3 to 2, so the system becomes more ordered and entropy decreases.
b. Yes. Even though ΔS_{system} is negative, the reaction releases a large amount of heat ($\Delta H < 0$), which increases the entropy of the surroundings. If this increase in $\Delta S_{\text{surroundings}}$ is greater than the decrease in ΔS_{system}, then the total entropy of the universe increases and the forward reaction is spontaneous.

Exercise $10.E.11$*****

a. $\Delta S_{\text{surr}} < 0$. In an endothermic reaction, heat is absorbed from the surroundings, decreasing the entropy of the surroundings.
b. $\Delta S_{\text{surr}} > 0$. In an exothermic reaction, heat is transferred from the system to the surroundings, increasing the entropy of the surroundings.

Exercise $10.E.12$*****

At 0 K, a perfect crystal would have no particle motion and a perfectly ordered arrangement of atoms. Because there is only one possible microstate, the entropy is zero.

Exercise $10.E.13$*****

$$\Delta S^\circ = \sum m\,S^\circ(\text{products}) - \sum n\,S^\circ(\text{reactants})$$

a. ΔS° is negative because a gas condenses to a liquid.

$$\Delta S^\circ = S^\circ(\mathrm{CS_2\,(l)}) - S^\circ(\mathrm{CS_2\,(g)}) = 151.3\ \mathrm{J/(mol\cdot K)} - 237.8\ \mathrm{J/(mol\cdot K)} = -86.5\ \mathrm{J/(mol\cdot K)}$$

b. ΔS° is positive because a gas is formed from a solid.

$$\Delta S^\circ = S^\circ(\mathrm{Cu\,(g)}) - S^\circ(\mathrm{Cu\,(s)}) = 166.4\ \mathrm{J/(mol\cdot K)} - 33.2\ \mathrm{J/(mol\cdot K)} = 133.2\ \mathrm{J/(mol\cdot K)}$$

c. ΔS° is negative because gases react to form a liquid.

$$\begin{aligned}\Delta S^\circ &= 2S^\circ(\mathrm{H_2O\,(l)}) - [2S^\circ(\mathrm{H_2\,(g)}) + S^\circ(\mathrm{O_2\,(g)})]\\ &= 2(70.0) - [2(130.7) + 205.2]\\ &= 140.0 - 466.6 = -326.6\ \mathrm{J/(mol\cdot K)}\end{aligned}$$

d. ΔS° is negative because 3 moles of gas form only 2 moles of gas.

$$\begin{aligned}\Delta S^\circ &= 2S^\circ(\mathrm{SO_3\,(g)}) - [2S^\circ(\mathrm{S\,(s)}) + 3S^\circ(\mathrm{O_2\,(g)})]\\ &= 2(256.8) - [2(32.1) + 3(205.2)]\\ &= 513.6 - [64.2 + 615.6] = 513.6 - 679.8 = -166.2\ \mathrm{J/(mol\cdot K)}\end{aligned}$$

e. ΔS° is negative because a gas is consumed and no gas is formed.

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2SO_4\,(aq)}) - [S^\circ(\mathrm{SO_3\,(g)}) + S^\circ(\mathrm{H_2O\,(l)})]\\ &= 20.1 - [256.8 + 70.0] = 20.1 - 326.8 = -306.7\ \mathrm{J/(mol\cdot K)}\end{aligned}$$

f. ΔS° is positive because gases are formed from a solid.

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{N_2O\,(g)}) + 2S^\circ(\mathrm{H_2O\,(g)}) - S^\circ(\mathrm{NH_4NO_3\,(s)})\\ &= 220.0 + 2(188.8) - 151.1\\ &= 220.0 + 377.6 - 151.1 = 446.5\ \mathrm{J/(mol\cdot K)}\end{aligned}$$

Exercise $10.E.14$**

$$\Delta G^\circ = \sum m\,\Delta G_f^\circ(\mathrm{products}) - \sum n\,\Delta G_f^\circ(\mathrm{reactants})$$

a.

$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ(\mathrm{NH_3\,(g)}) - [\Delta G_f^\circ(\mathrm{N_2\,(g)}) + 3\Delta G_f^\circ(\mathrm{H_2\,(g)})]\\ &= 2(-16.4\ \mathrm{kJ/mol}) - [0 + 3(0)]\\ &= -32.8\ \mathrm{kJ/mol}\end{aligned}$$

Spontaneous ($\Delta G < 0$)

b.

$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ(\mathrm{HBr\,(g)}) - [\Delta G_f^\circ(\mathrm{H_2\,(g)}) + \Delta G_f^\circ(\mathrm{Br_2\,(l)})]\\ &= 2(-53.4) - [0 + 0]\\ &= -106.8\ \mathrm{kJ/mol}\end{aligned}$$

Spontaneous ($\Delta G < 0$)

c.

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ(\mathrm{Mn\,(s)}) + \Delta G_f^\circ(\mathrm{O_2\,(g)}) - \Delta G_f^\circ(\mathrm{MnO_2\,(s)})\\ &= 0 + 0 - (-465.1)\\ &= 465.1\ \mathrm{kJ/mol}\end{aligned}$$

Nonspontaneous ($\Delta G > 0$)

Exercise $10.E.15$**

(a) At 298 K, ΔG° can be found either by using ΔG_f° values:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ(\mathrm{CaO\,(s)}) + \Delta G_f^\circ(\mathrm{CO_2\,(g)}) - \Delta G_f^\circ(\mathrm{CaCO_3\,(s)})\\ &= (-603.3) + (-394.4) - (-1129.1)\\ &= 131.4\ \mathrm{kJ/mol}\end{aligned}$$

Or by finding ΔH° and ΔS°:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\mathrm{CaO\,(s)}) + \Delta H_f^\circ(\mathrm{CO_2\,(g)}) - \Delta H_f^\circ(\mathrm{CaCO_3\,(s)})\\ &= (-634.9) + (-393.5) - (-1207.6)\\ &= 179.2\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{CaO\,(s)}) + S^\circ(\mathrm{CO_2\,(g)}) - S^\circ(\mathrm{CaCO_3\,(s)})\\ &= 38.1 + 213.8 - 91.7\\ &= 160.2\ \mathrm{J/(mol\cdot K)}\end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 179.2\ \mathrm{kJ/mol} - 298\,\mathrm{K}(160.2\ \mathrm{J/(mol\cdot K)})\left(\frac{\mathrm{kJ}}{1000\ \mathrm{J}}\right) = 131.5\ \mathrm{kJ/mol}$$

(b) Since ΔG° is temperature-dependent, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ must be used to find ΔG° at 1225 K:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 179.2\ \mathrm{kJ/mol} - 1225\,\mathrm{K}(160.2\ \mathrm{J/(mol\cdot K)})\left(\frac{\mathrm{kJ}}{1000\ \mathrm{J}}\right) = -17.0\ \mathrm{kJ/mol}$$

(c) For this reaction, both ΔH° and ΔS° are positive. Using the Gibbs free energy equation:

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

At low temperatures, the ΔH° term dominates, so ΔG° is positive and the reaction is nonspontaneous.

At higher temperatures, the $T\Delta S^\circ$ term becomes large enough to outweigh ΔH°. As a result, ΔG° becomes negative, and the reaction becomes spontaneous.

In summary, the reaction becomes spontaneous at higher temperatures because it is entropy-driven: the positive entropy change favours the reaction as temperature increases.

Exercise $10.E.16$**

The reaction switches from nonspontaneous to spontaneous when $\Delta G^\circ = 0$:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{179.2\ \text{kJ/mol}\left(\frac{1000\ \text{J}}{\text{kJ}}\right)}{160.2\ \text{J/(mol}\cdot\text{K)}} = 1119\ \text{K}$$

At temperatures above 1119 K, the reaction becomes spontaneous under standard state conditions.

Exercise $10.E.17$**

ΔS° is positive because a gas is produced from solid reactants. The reaction is endothermic ($\Delta H^\circ > 0$). Therefore, the reaction will be spontaneous only at higher temperatures, where the $T\Delta S^\circ$ term is large enough to overcome the positive enthalpy.

Exercise $10.E.18$***

a) $\Delta S^\circ < 0$ because the number of particles decreases — six separate atoms become three molecules, leading to a more ordered system.
$\Delta H^\circ < 0$ because bonds are being formed, which releases energy.

(b) The reaction is spontaneous only at lower temperatures. Since $\Delta H^\circ < 0$ (exothermic) and $\Delta S^\circ < 0$, the enthalpy change favours spontaneity, but the entropy change does not. According to the Gibbs free energy equation, this combination results in spontaneity only when the temperature is low enough that the $T\Delta S^\circ$ term doesn't dominate.

Exercise $10.E.19$**

$\Delta S^\circ > 0$ because a gas is formed. The reaction is also exothermic ($\Delta H^\circ < 0$). Since both $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$, $\Delta G^\circ < 0$ at all temperatures. Therefore, the reaction is spontaneous at all temperatures.

Exercise $10.E.20$**

(a)

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(\text{AlCl}_3\,(\text{s})) - [2\Delta H_f^\circ(\text{Al}\,(\text{s})) + 3\Delta H_f^\circ(\text{Cl}_2\,(\text{g}))] \\ &= 2(-704.2\ \text{kJ/mol}) \\ &= -1408.4\ \text{kJ/mol}\end{aligned}$$
$$\begin{aligned}\Delta S^\circ &= 2S^\circ(\text{AlCl}_3(s)) - [2S^\circ(\text{Al}\,(\text{s})) + 3S^\circ(\text{Cl}_2\,(\text{g}))] \\ &= 2(109.3\ \text{J/(mol}\cdot\text{K)}) - [2(28.3\ \text{J/(mol}\cdot\text{K)}) + 3(223.1\ \text{J/(mol}\cdot\text{K)})] \\ &= -507.3\ \text{J/(mol}\cdot\text{K)}\end{aligned}$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -1408.4\ \text{kJ/mol} - 298K(-507.3\ \text{J/(mol}\cdot\text{K)})\left(\frac{\text{kJ}}{1000\ \text{J}}\right) = -1257.2\ \text{kJ/mol}$$

The reaction is spontaneous at 298 K.

(b) The reaction switches from spontaneous to nonspontaneous when $\Delta G^\circ = 0$:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-1408.4\ \text{kJ/mol}\left(\frac{1000\ \text{J}}{\text{kJ}}\right)}{-507.3\ \text{J/(mol}\cdot\text{K)}} = 2776\ \text{K}$$

At temperatures above 2776 K, the reaction becomes nonspontaneous under standard state conditions.

Exercise $10.E.21$**

(a) Add the two reactions and cancel $\text{H}_2\,(\text{g})$:

$$2\,\text{CH}_4\,(\text{g}) + \frac{1}{2}\text{O}_2\,(\text{g}) \longrightarrow \text{C}_2\text{H}_6\,(\text{g}) + \text{H}_2\text{O}\,(\text{g})$$

(b)

$$\Delta G^\circ = +68.1\ \text{kJ/mol} + (-228.6\ \text{kJ/mol}) = -160.5\ \text{kJ/mol}$$

(c) Yes, the overall reaction is spontaneous under standard conditions because the total ΔG° is negative. The formation of water provides enough free energy to drive the otherwise nonspontaneous conversion of methane.

Exercise $10.E.22$**

(a)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 100\ \text{kJ/mol} - 298\,K(250\ \text{J/(mol}\cdot\text{K)})\left(\frac{\text{kJ}}{1000\ \text{J}}\right) = 25.5\ \text{kJ/mol}$$

At 298 K, the reaction is nonspontaneous.

(b)

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{100\ \text{kJ/mol}\left(\frac{1000\ \text{J}}{\text{kJ}}\right)}{250\ \text{J/(mol}\cdot\text{K)}} = 400\ \text{K}$$

The reaction is spontaneous above 400 K.

(c)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 100\ \text{kJ/mol} - 650\,\text{K}(250\ \text{J/(mol}\cdot\text{K)})\left(\frac{\text{kJ}}{1000\ \text{J}}\right) = -62.5\ \text{kJ/mol}$$

At 650 K, the reaction is spontaneous.

Exercise $10.E.23$**

No, ΔG° refers to standard conditions. A reaction with $\Delta G^\circ < 0$ is nonspontaneous ($\Delta G > 0$) under nonstandard conditions when $Q > K$.

Exercise $10.E.24$**

(a) $Q < K, \Delta G < 0$

(b) $Q = K, \Delta G = 0$

(c) $Q > K, \Delta G > 0$

Exercise $10.E.25$**

A large K value means that the reaction mixture contains mostly products. However, if the reaction mixture already has more products than it would at equilibrium ($Q > K$), the forward reaction will not be spontaneous ($\Delta G > 0$). The reverse reaction will proceed to reach equilibrium.

Exercise $10.E.26$*

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$Q = \frac{P_{H_2O}^2}{P_{H_2}^2 P_{O_2}}$$

$$\Delta G = -457.18 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}}\right)\left(\frac{\text{kJ}}{1000\ \text{J}}\right)(298\ \text{K}) \ln\left(\frac{(0.010)^2}{(2.0)^2(2.0)}\right) = -485\ \text{kJ/mol}$$

Exercise $10.E.27$*

(a)

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$Q = \frac{P_{H_2O}}{P_{CO_2}}$$

$$\Delta G = -79 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}}\right)\left(\frac{\text{kJ}}{1000\ \text{J}}\right)(298\ \text{K}) \ln\left(\frac{0.10}{2.0}\right) = -86\ \text{kJ/mol}$$

The reaction is spontaneous under these conditions.

(b)

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$Q = \frac{P_{H_2O}}{P_{CO_2}}$$

$$\Delta G = -79 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}}\right)\left(\frac{\text{kJ}}{1000\ \text{J}}\right)(298\ \text{K}) \ln\left(\frac{2.0}{0.00010}\right) = -54\ \text{kJ/mol}$$

The reaction is spontaneous under these conditions. The smaller negative value of ΔG indicates that the reaction is closer to equilibrium than in part (a).

Exercise $10.E.28$*

Use the relationship:

$$\Delta G^\circ = -RT \ln K$$

Rearranged:

$$K = e^{-\frac{\Delta G^\circ}{RT}}$$

(a)

$$K = e^{-\frac{-9.2\ \text{kJ/mol}}{\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(298\ \text{K})}\left(\frac{1000\ \text{J}}{\text{kJ}}\right)} = 41$$

(b)

$$K = e^{-\frac{7.3\ \text{kJ/mol}}{\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(298\ \text{K})}\left(\frac{1000\ \text{J}}{\text{kJ}}\right)} = 0.053$$

(c)

$$K = e^{-\frac{-79\ \text{kJ/mol}}{\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(298\ \text{K})}\left(\frac{1000\ \text{J}}{\text{kJ}}\right)} = 7.0 \times 10^{13}$$

Exercise $10.E.29$**

Step 1: Calculate ΔH°:

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(\text{Fe(s)}) + 3\Delta H_f^\circ(\text{CO}_2\text{(g)}) - [\Delta H_f^\circ(\text{Fe}_2\text{O}_3\text{(s)}) + 3\Delta H_f^\circ(\text{CO(g)})] \\ &= 2(0\ \text{kJ/mol}) + 3(-393.5\ \text{kJ/mol}) - [1(-842.2\ \text{kJ/mol}) + 3(-110.5\ \text{kJ/mol})] \\ &= -6.8\ \text{kJ/mol}\end{aligned}$$

Step 2: Calculate ΔS°:

$$\begin{aligned}\Delta S^\circ &= 2S^\circ(\text{Fe(s)}) + 3S^\circ(\text{CO}_2\text{(g)}) - [S^\circ(\text{Fe}_2\text{O}_3\text{(s)}) + 3S^\circ(\text{CO(g)})] \\ &= 2(27.3\ \text{J/(mol·K)}) + 3(213.8\ \text{J/(mol·K)}) - [1(87.4\ \text{J/(mol·K)}) + 3(197.7\ \text{J/(mol·K)})] \\ &= 15.5\ \text{J/(mol·K)}\end{aligned}$$

Step 3: Calculate ΔG° at 298 K:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -6.8\ \text{kJ/mol} - 298\ \text{K}(15.5\ \text{J/(mol·K)})\left(\frac{\text{kJ}}{1000\ \text{J}}\right) = -11.4\ \text{kJ/mol}$$

Step 4: Calculate K:

$$K = e^{-\frac{-11.4\ \text{kJ/mol}}{\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(298,\text{K})}\left(\frac{1000\ \text{J}}{\text{kJ}}\right)} = 100$$

Exercise $10.E.30$*

$$\Delta G^\circ = -RT \ln K$$

(a)

$$\Delta G^\circ = -\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)(2273\ \text{K})\left(\frac{\text{kJ}}{1000\ \text{J}}\right)\ln(4.1 \times 10^{-4}) = 147\ \text{kJ/mol}$$

(b)

$$\Delta G^\circ = -\left(8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(673\text{ K})\left(\frac{\text{kJ}}{1000\text{ J}}\right)\ln(50) = -21.9\text{ kJ/mol}$$

(c)

$$\Delta G^\circ = -\left(8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(1253\text{ K})\left(\frac{\text{kJ}}{1000\text{ J}}\right)\ln(1.67) = -5.34\text{ kJ/mol}$$

(d)

$$\Delta G^\circ = -\left(8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298\text{ K})\left(\frac{\text{kJ}}{1000\text{ J}}\right)\ln(3.3\times10^{-13}) = 71\text{ kJ/mol}$$

Exercise $10.E.31$***

(a) Yes. Since the reaction is endothermic ($\Delta H^\circ > 0$) with increasing entropy ($\Delta S^\circ > 0$), the reaction is nonspontaneous at lower temperatures but becomes spontaneous at higher temperatures. Increasing temperature increases the value of $T\Delta S^\circ$, which favours spontaneity.

(b)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 179.2\text{ kJ/mol} - (1225\text{ K})\,(160.2\text{ J/(mol·K)})\left(\frac{\text{kJ}}{1000\text{ J}}\right) = -17.0\text{ kJ/mol}$$

(c) Since $\Delta G^\circ < 0$, the reaction is product-favoured at 1225 K. Therefore, $K > 1$.

(d)

$$\Delta G^\circ = -RT\ln K \quad \Rightarrow \quad \ln K = -\frac{\Delta G^\circ}{RT}$$

$$\ln K = -\frac{-17.0\text{ kJ/mol}(1000\text{ J/kJ})}{(8.314\text{ J/mol·K})(1225\text{ K})} = \frac{17000\text{ J/mol}}{(10184.65\text{ J/mol})} = 1.67$$

$$K = e^{1.67} = 5.3$$

(e) Since the only gas in the equilibrium expression is CO_2, and the solids are not included in K_p, we have:

$$K_p = P_{\text{CO}_2} = 5.3\text{ atm}$$

Exercise $10.E.32$*

ΔG < 0 because the process is spontaneous.

ΔH > 0 because energy is required to overcome intermolecular forces as the solid melts.

ΔS > 0 because particles in a liquid have more freedom of motion than in a solid, resulting in an increase in entropy.

Exercise $10.E.33$**

(a)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 28.16\text{ kJ/mol} - (575\text{ K})\,(26.22\text{ J/(mol·K)})\left(\frac{\text{kJ}}{1000\text{ J}}\right) = 13.08\text{ kJ/mol}$$

Since ΔG° > 0, melting is nonspontaneous at 575 K.

(b) At the melting point, the solid and liquid are in equilibrium, so $\Delta G^\circ = 0$:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T_{\text{melt}} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{28.16\text{ kJ/mol}\left(\frac{1000\text{ J}}{\text{kJ}}\right)}{26.22\text{ J/(mol}\cdot\text{K)}} = 1074\text{ K}$$

The melting point of NaCl is 1074 K. Above 1074 K, NaCl melts spontaneously.

Exercise $10.E.34$**

Step 1: Calculate ΔH°:

$$\begin{aligned}\Delta H^\circ &= 1\Delta H_f^\circ(\text{Br}_2\,(\text{g})) - 1\Delta H_f^\circ(\text{Br}_2\,(\text{l}))\\ &= 1(30.9\text{ kJ/mol}) - 1(0\text{ kJ/mol})\\ &= 30.9\text{ kJ/mol}\end{aligned}$$

Step 2: Calculate ΔS°:

$$\begin{aligned}\Delta S^\circ &= 1S^\circ(\text{Br}_2\,(\text{g})) - 1S^\circ(\text{Br}_2\,(\text{l}))\\ &= 1(245.5\text{ J/(mol}\cdot\text{K)}) - 1(152.2\text{ J/(mol}\cdot\text{K)})\\ &= 93.3\text{ J/(mol}\cdot\text{K)}\end{aligned}$$

Step 3: At the boiling point, the vapour and liquid are in equilibrium, so $\Delta G^\circ = 0$:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T_{\text{boil}} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{30.9\text{ kJ/mol}\left(\frac{1000\text{ J}}{\text{kJ}}\right)}{93.3\text{ J/(mol}\cdot\text{K)}} = 331\text{ K}$$

Exercise $10.E.35$*

Vapour pressure increases with increasing temperature. As temperature rises, a greater fraction of molecules in the liquid have enough kinetic energy to overcome intermolecular forces and escape into the gas phase, increasing the number of gas-phase molecules and the resulting vapour pressure.

Exercise $10.E.36$**

(a) PH_3 Although both molecules are polar, NH_3 can form hydrogen bonds due to the presence of $\text{N}-\text{H}$ bonds, while PH_3 cannot. Hydrogen bonding gives NH_3 stronger intermolecular forces, which lowers its vapour pressure relative to PH_3.

(b) $\text{CH}_3\text{CH}_2\text{Cl}$

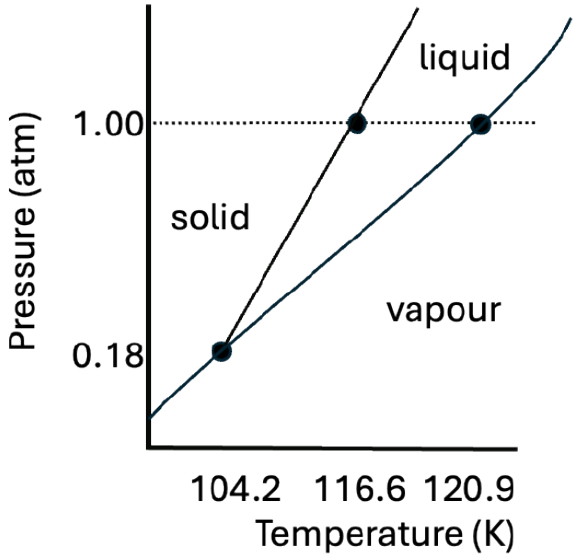
$\text{CH}_3\text{CH}_2\text{OH}$ can hydrogen-bond, while $\text{CH}_3\text{CH}_2\text{Cl}$ cannot. Hydrogen bonding results in stronger intermolecular forces in $\text{CH}_3\text{CH}_2\text{OH}$, so fewer molecules escape into the gas phase, leading to a lower vapour pressure compared to $\text{CH}_3\text{CH}_2\text{Cl}$.

Exercise $10.E.37$*

1. (a) i (b) iii (c) v (d) ii (e) iv

2. During melting and boiling, the added heat is used to overcome intermolecular forces, not to increase kinetic energy. As a result, the temperature stays constant until the phase change is complete.

Exercise $10.E.38$**



Solid krypton is more dense than liquid krypton because the melting curve has a positive slope. This indicates that increasing pressure favours the solid phase, meaning the solid occupies less volume than the same amount of liquid.

Exercise $10.E.39$*

(a) The maximum pressure at which ice and water vapour can coexist in equilibrium is at the triple point, which occurs at 0.006 atm. Above this pressure, any transition from solid to gas must pass through the liquid phase.

(b) At 50 °C and 0.006 atm, the water exists as vapour. As the pressure increases to 10 atm at constant temperature, the water vapour condenses to form liquid water.

(c) At 200 °C and 1.0 atm, the water is in the vapour phase. As it is cooled at constant pressure:

- It condenses to liquid at 100 °C (normal boiling point),
- It freezes to solid at 0 °C (normal melting point),
- It remains solid as the temperature decreases to –10 °C.

Exercise $10.E.40$***

ΔG is the free energy change under any conditions. It depends on the temperature and the actual concentrations or partial pressures of reactants and products. A negative value indicates that the forward reaction is spontaneous under the current conditions.

ΔG° is the standard free energy change. It refers to the free energy change when all reactants and products are in their standard states (1 atm pressure for gases, 1 M concentration for solutions), usually at 298 K. It reflects the spontaneity of a reaction under standard conditions and is often used to calculate equilibrium constants.

ΔG° at 500 K still assumes standard states, but the temperature is different. Its value differs from ΔG° at 298 K because Gibbs free energy depends on temperature through the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Even if ΔH° and ΔS° do not change significantly with temperature, the term $T\Delta S^\circ$ can have a large effect. As a result, the sign or magnitude of ΔG° may change at higher or lower temperatures.

Exercise $10.E.41$**

Vaporization requires a complete separation of particles into the gas phase, which involves fully overcoming the intermolecular forces holding the particles together. In contrast, fusion (melting) only requires enough energy for particles to move past one another in the liquid phase, while still remaining relatively close. Because vaporization involves a greater disruption of intermolecular forces than fusion, the enthalpy change for vaporization is larger: $\Delta H_{\text{vap}} > \Delta H_{\text{fus}}$.

Exercise $10.E.42$***

The dissolution equilibrium is:

$$\mathrm{Ag_2S\,(s) \rightleftharpoons 2\,Ag^+\,(aq) + S^{2-}\,(aq)}$$

Step 1: Use the relationship $\Delta G^\circ = -RT\ln K$ to find the standard free energy change for the dissolution.

$$\Delta G^\circ = -(8.314\ \text{J/mol·K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)(298\ \text{K})\ln(8\times10^{-51}) = 285.8\ \text{kJ/mol}$$

Step 2: Relate the ΔG° for the dissolution to standard free energies of formation:

$$\Delta G^\circ = \Delta G_\text{f}^\circ(2\,\mathrm{Ag^+}) + \Delta G_\text{f}^\circ(\mathrm{S^{2-}}) - \Delta G_\text{f}^\circ(\mathrm{Ag_2S\,(s)})$$

$$285.8\ \text{kJ/mol} = 2(77.1\ \text{kJ/mol}) + \Delta G_f^\circ(\mathrm{S^{2-}}) - (-39.5\ \text{kJ/mol})$$

$$\Delta G_f^\circ(S^{2-}) = 285.8\ \text{kJ/mol} - 193.7\ \text{kJ/mol} = 92.1\ \text{kJ/mol}$$

Exercise $10.E.43$***

Step 1: Convert masses to moles

$$\text{Molar mass of } SbCl_5 = 299.0\ \text{g/mol} \quad \Rightarrow \quad n_{SbCl_5} = \frac{3.43\ \text{g}}{299.0\ \text{g/mol}} = 0.01147\ \text{mol}$$

$$\text{Molar mass of } SbCl_3 = 228.1\ \text{g/mol} \quad \Rightarrow \quad n_{SbCl_3} = \frac{9.14\ \text{g}}{228.1\ \text{g/mol}} = 0.04007\ \text{mol}$$

$$\text{Molar mass of } Cl_2 = 70.9\ \text{g/mol} \quad \Rightarrow \quad n_{Cl_2} = \frac{2.84\ \text{g}}{70.9\ \text{g/mol}} = 0.04006\ \text{mol}$$

Step 2: Calculate partial pressures using the ideal gas law

Use $P = \frac{nRT}{V}$, with:

- $R = 0.08206\ \text{L·atm/(mol·K)}$
- $T = 448^\circ\text{C} = 721\ \text{K}$
- $V = 5.00\ \text{L}$

$$P_{SbCl_5} = \frac{(0.01147\ \text{mol})(0.08206\ \text{L·atm/mol·K})(721\ \text{K})}{5.00\ \text{L}} = 0.1357\ \text{atm}$$

$$P_{SbCl_3} = \frac{(0.04007\ \text{mol})(0.08206\ \text{L·atm/mol·K})(721\ \text{K})}{5.00\ \text{L}} = 0.4742\ \text{atm}$$

$$P_{Cl_2} = \frac{(0.04006\ \text{mol})(0.08206\ \text{L·atm/mol·K})(721\ \text{K})}{5.00\ \text{L}} = 0.4740\ \text{atm}$$

Step 3: Write the equilibrium expression and solve for K_p

$$K_p = \frac{P_{SbCl_3} \cdot P_{Cl_2}}{P_{SbCl_5}} = \frac{(0.4742\ \text{atm})(0.4740\ \text{atm})}{0.1357\ \text{atm}} = 1.656$$

Step 4: Calculate ΔG° from K_p

Use $\Delta G^\circ = -RT\ln K$, with:

- $R = 8.314\ \text{J/(mol·K)}$
- $T = 721\ \text{K}$
- $K_p = 1.656$

$$\Delta G^\circ = -(8.314\ \text{J/mol·K})(721\ \text{K})\ln(1.656) \cdot \frac{1\ \text{kJ}}{1000\ \text{J}}$$
$$= -3023.6\ \text{J/mol} = \boxed{-3.02\ \text{kJ/mol}}$$

The negative value of ΔG° indicates that the decomposition of $SbCl_5$ is slightly spontaneous under standard conditions at 448 °C.

Exercise $10.E.44$***

ΔG is negative because the process is spontaneous.

ΔH is positive because the solution feels cold, indicating that energy is absorbed from the surroundings (the process is endothermic).

ΔS is positive. For the process to be spontaneous, it must occur with an increase in entropy since the process is endothermic.

Exercise $10.E.45$***

(a)

$$\Delta G^\circ = 2\Delta G_f^\circ(\text{Cu(s)}) + 1\Delta G_f^\circ(\text{S(s)}) - \Delta G_f^\circ(\text{Cu}_2\text{S(s)})$$
$$= 0\ \text{kJ/mol} + 0\ \text{kJ/mol} - (-86.2\ \text{kJ/mol})$$
$$= 86.2\ \text{kJ/mol}$$

(b) $\text{S(s)} + \text{O}_2\text{(g)} \rightleftharpoons \text{SO}_2\text{(g)}$

$$\Delta G^\circ = 1\Delta G_f^\circ(\text{SO}_2\text{(g)}) - [1\Delta G_f^\circ(\text{S(s)}) + 1\Delta G_f^\circ(\text{O}_2\text{(s)})]$$
$$= -300.1\ \text{kJ/mol} - [0\ \text{kJ/mol} + (0\ \text{kJ/mol})]$$
$$= -300.1\ \text{kJ/mol}$$

(c)

$$\text{Cu}_2\text{S(s)} \rightleftharpoons 2\,\text{Cu(s)} + \cancel{\text{S(s)}} \qquad \Delta G^\circ = 86.2\ \text{kJ/mol}$$
$$\cancel{\text{S(s)}} + \text{O}_2\text{(g)} \rightleftharpoons \text{SO}_2\text{(g)} \qquad \Delta G^\circ = -300.1\ \text{kJ/mol}$$
$$\text{Cu}_2\text{S(s)} + \text{O}_2\text{(g)} \rightleftharpoons 2\,\text{Cu(s)} + \text{SO}_2\text{(g)} \qquad \Delta G^\circ = 86.2 + (-300.1) = -213.9\ \text{kJ/mol}$$

The overall ΔG° is negative, so the coupled reaction proceeds spontaneously under standard state conditions. Coupling the decomposition of Cu_2S with the oxidation of sulfur makes the overall process thermodynamically favourable, enabling efficient copper production.

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11.1: Introduction

The Economical Impact of Corrosion

When we think of chemistry's impact on the world, we often imagine high-tech discoveries, but sometimes it can be about protecting the materials we depend upon. Dr. Faiza Al-Kharafi, a pioneering electrochemist from Kuwait, built her career around understanding and preventing corrosion: the slow, often invisible electrochemical process that causes metals to degrade.



Figure 11.1.1**:** A graphic with basic facts about Faiza Al-Kharafi, an electrochemist who has explored the behaviour of corrosion extreme conditions such as pH, salinity, and temperature, as well as ways to prevent it. She is the first woman to head a ma university in the Middle East. Image reproduced with permission, copyright Eric Ramahatra for Women in Science 2011 - Kuwa

We all recognize corrosion: rust forming on a car, or the green roofs of the Parliament Buildings in Ottawa. In both cases, a metal (iron in the car, copper on the roofs) undergoes oxidation, meaning it loses electrons over time. Corrosion occurs when a metal reacts with substances like oxygen and moisture, forming metal oxides. This process can be accelerated by factors like temperature, salt, and pH. While corrosion is natural, preventing it is critical to extending the lifetime of materials.

As the first woman to lead a major university in the Middle East, Dr. Al-Kharafi focused her research on understanding corrosion in harsh environments, especially those found in the oil and gas industry. She studied how high temperatures, salinity, and pH affect corrosion rates in metals like aluminum, steel, and copper alloys. Her work helped explain how chloride ions in seawater accelerate corrosion and led to improved corrosion inhibitors. For example, she reported that an organic molecule, 5-phenyl-1-H-tetrazole, was able to inhibit the corrosion of copper up to 97% in high-salt solutions that mimic seawater. Her research has led to more effective materials for pipelines, desalination plants, heat exchangers, and water treatment infrastructure.



Figure 11.1.2**:** Water pipe that shows signs of rust and corrosion. Stock image reproduced with permission under Pixabay Content Lic

Though based in Kuwait, Al-Kharafi's work addresses a global problem. In Canada, for example, our roads are salted in winter, our bridges face freeze-thaw cycles, and our energy and water infrastructure span vast, sometimes remote regions. Replacing corroded components is expensive: corrosion costs Canada over $50 billion USD annually (almost 3% of our GDP), affecting everything from municipal water pipes in Toronto to oil pipelines in Alberta. Managing corrosion is an economic and environmental priority. Dr. Al-Kharafi's leadership in corrosion research serves as a reminder that scientific innovation solves problems on the global scale.

In this chapter, we'll explore corrosion in more detail, along with the fundamentals of electrochemistry: how redox reactions generate electricity in batteries and galvanic cells, and how electrical energy can drive chemical reactions in electrolysis systems.

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11.2: Review of Redox Chemistry

Learning Objectives

- Describe what happens during a redox reaction, and identify which species are oxidized and which are reduced.
- Identify oxidizing and reducing agents in redox reactions.
- Assign oxidation numbers to elements in compounds and ions to help recognize redox reactions.
- Balance redox reactions in acidic and basic solutions using the half-reaction method, ensuring conservation of both mass and charge.

Electrochemistry is the study of the relationship between chemical reactions and electron flow. At its core are oxidation-reduction (redox) reactions, a broad class of reactions that involve the transfer of electrons. These processes play a central role in our everyday life, from corrosion and metal refining to rechargeable batteries and biological energy conversion. For example, electric vehicles (Figure 11.2.1) rely on batteries powered by redox reactions that release energy in a controlled, useful form.

To understand how chemical energy is converted to electrical energy, and vice versa, we need a clear picture of redox reactions.



Figure 11.2.1: Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

Redox Reactions

In a redox reaction, one substance loses electrons (oxidation) and another gains electrons (reduction). Because electrons must be transferred from one substance to another, oxidation and reduction reactions always occur together.

Oxidation (electron loss by Zn): $\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-}$

Reduction (electron gain by $\mathrm{Cu^{2+}}$): $\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Cu(s)}$

Overall reaction: $\mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)}$

The reducing agent is the species that provides electrons to the other reactant and is itself oxidized. In this example, Zn is the reducing agent because it loses the electrons, which reduce $\mathrm{Cu^{2+}}$.

The oxidizing agent is the species that accepts electrons from the other reactant and is itself reduced. Here, $\mathrm{Cu^{2+}}$ is the oxidizing

agent because it gains electrons from Zn.

Note

Oxidation is the loss of electrons.

Reduction is the gain of electrons.

Two memory aids to keep oxidation and reduction straight:

- **LEO the lion says GER**: **L**oss of **E**lectrons **O**xidation; **G**ain **E**lectrons **R**eduction.
- **OIL RIG**: **O**xidation **I**s **L**oss; **R**eduction **I**s **G**ain.



Sometimes it is easy to identify which substances are being oxidized and reduced, especially when neutral atoms form ions, but in more complex reactions, it is not always obvious. To help track the flow of electrons, chemists assign oxidation numbers, which are introduced next.

Oxidation Numbers

Oxidation numbers (or oxidation states) are a bookkeeping tool that chemists use to keep track of electron transfer in chemical reactions. They are assigned to atoms in molecules or ions based on a set of rules and help identify which atoms are oxidized (an increase in oxidation number) and which are reduced (a decrease in oxidation number). Oxidation numbers do not always represent actual ionic charges; rather they are a convenient way of following the electrons in a redox reaction.

Rules for Assigning Oxidation Numbers:

1. An atom in its elemental form has an oxidation number of 0.

    Examples: $\mathrm{Zn\,(s)}$, $\mathrm{O_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ all have an oxidation number = 0.

2. A monoatomic ion has an oxidation number equal to its charge.

    Examples: $\mathrm{Zn^{2+}}$ = +2, $\mathrm{Na^{+}}$ = +1, $\mathrm{Cl^{-}}$ = -1, $\mathrm{O^{2-}}$ = -2.

3. The sum of the oxidation numbers in a neutral molecule is 0.

4. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.

    Example: The sum of the oxidation numbers in $\mathrm{{SO_4}^{2-}}$ is equal to -2.

5. Hydrogen has an oxidation number of +1 when bonded to nonmetals (e.g. in $\mathrm{H_2O}$) and -1 when bonded to metals and boron (e.g. in NaH).

6. Oxygen usually has an oxidation number of -2, except when two oxygen atoms share a single bond in compounds called peroxides (e.g. $\mathrm{H_2O_2}$) where it is -1.

7. Other atoms usually have the oxidation number corresponding to their most common ionic charge.

    Example: In $\mathrm{AlCl_3}$, Al has an oxidation number of +3 and each Cl has an oxidation number of -1.

Example 11.2.1

Assign oxidation numbers to each atom in the following substances:

a) $\mathrm{HNO_3}$ b) $\mathrm{S_2O_3^{2-}}$

Solution

a) H is +1 (in compound with non-metal) and O is -2.

The sum of oxidation numbers must be 0, so let x = oxidation number of N:

$$\underbrace{(+1)}_{\mathrm{H}} + \underbrace{x}_{\mathrm{N}} + 3\underbrace{(-2)}_{\mathrm{O}} = \underbrace{0}_{\text{total}}$$
$$x = 5$$

N is +5.

b) O is -2.

The sum of the oxidation numbers is the charge of the ion, so let x = oxidation number of S:

$$2\underbrace{x}_{\mathrm{S}} + 3\underbrace{(-2)}_{\mathrm{O}} = \underbrace{-2}_{\text{total}}$$
$$x = 2$$

S is +2.

Exercise 11.2.1

Assign oxidation numbers to each atom in the following substances:

a) $\mathrm{KClO_3}$ b) $\mathrm{SO_4^{2-}}$

Answer available at the end of this section.

Oxidation numbers can be used to determine which substance is oxidized and which is reduced in a chemical reaction.

- Oxidation is the loss of electrons (negatively charged), so the oxidation number of the atom increases with oxidation.
- Reduction is the gain of electrons, so the oxidation number of the atom decreases with reduction.

The substance that is oxidized is the reducing agent (it donates electrons), and the substance that is reduced is the oxidizing agent (it accepts electrons). If the oxidation numbers of all atoms stay the same in a reaction, then no electrons are transferred, and the reaction is not a redox reaction.

Example 11.2.2

Use oxidation numbers to determine which of the following are redox reactions. For each redox reaction, identify the oxidizing and reducing agents.

a) $\mathrm{Ca\,(s) + Sn^{2+}\,(aq) \rightarrow Ca^{2+}\,(aq) + Sn\,(s)}$

b) $\mathrm{CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g)}$

c) $\mathrm{HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)}$

Solution

The first step is to assign oxidation numbers to each reactant and product. After, look for changes in oxidation number for each atom.

a) $\overset{0}{\mathrm{Ca}}(\mathrm{s}) + \overset{+2}{\mathrm{Sn}^{2+}}(\mathrm{aq}) \rightarrow \overset{+2}{\mathrm{Ca}^{2+}}(\mathrm{aq}) + \overset{0}{\mathrm{Sn}}(\mathrm{s})$

Ca goes from 0 to +2, which means Ca has lost electrons (oxidation) and is the reducing agent.

Sn goes from +2 to 0, which means Sn^{2+} has gained electrons (reduction) and is the oxidizing agent.

b) $\overset{-4+1}{\mathrm{C}}\mathrm{H}_4(\mathrm{g}) + 2\,\overset{0}{\mathrm{O}}_2(\mathrm{g}) \rightarrow \overset{+4-2}{\mathrm{C}}\mathrm{O}_2(\mathrm{g}) + \overset{+1\ -2}{\mathrm{H}_2}\mathrm{O}(\mathrm{g})$

C goes from -4 to +4, which means it has lost electrons (oxidation) and is the reducing agent.

O goes from 0 to -2, so it has gained electrons (reduction) and is the oxidizing agent.

c) $\overset{+1-1}{\mathrm{HCl}}(\mathrm{aq}) + \overset{+1\ -2+1}{\mathrm{NaOH}}(\mathrm{aq}) \rightarrow \overset{+1\ -1}{\mathrm{NaCl}}(\mathrm{aq}) + \overset{+1\ -2}{\mathrm{H_2O}}(\mathrm{l})$

None of the atoms have changed in oxidation number, so this is not a redox reaction.

Exercise 11.2.2

Use oxidation numbers to determine which are redox reactions. For each redox reaction, identify the oxidizing and reducing agents.

a) $\mathrm{Cu}(\mathrm{s}) + 2\,\mathrm{Ag}^+(\mathrm{aq}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq}) + 2\,\mathrm{Ag}(\mathrm{s})$

b) $\mathrm{FeCl_2}(\mathrm{aq}) + 2\,\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{Fe(OH)_2}(\mathrm{s}) + 2\,\mathrm{NaCl}(\mathrm{aq})$

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

Answer available at the end of this section.

Balancing Redox Equations

In the reaction between copper metal and silver ions:

$$\mathrm{Cu}(\mathrm{s}) + \mathrm{Ag}^+(\mathrm{aq}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq}) + \mathrm{Ag}(\mathrm{s})$$

The equation is balanced in terms of atoms: there is one Cu atom and one Ag atom on each side. However, the reaction is not balanced in terms of charge. On the left side, the total charge is +1 (from Ag^+); on the right, the total charge is +2 (from Cu^{2+}). This imbalance tells us that electrons must be involved.

To balance a redox reaction, we need to track not only the atoms, but also the electrons transferred. We can do this by dividing the reaction into two half-reactions: one showing the oxidation (electron loss) and one showing the reduction (electron gain).

Oxidation half-reaction (electron loss): $\mathrm{Cu}(\mathrm{s}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq}) + 2\,\mathrm{e}^-$
Reduction half-reaction (electron gain):$\mathrm{Ag}^+(\mathrm{aq}) + \mathrm{e}^- \rightarrow \mathrm{Ag}(\mathrm{s})$

To balance the electrons, multiply the silver half-reaction by 2 so that both half-reactions involve 2 electrons:

$2\,\mathrm{Ag}^+(\mathrm{aq}) + 2\,\mathrm{e}^- \rightarrow 2\,\mathrm{Ag}(\mathrm{s})$

Adding the two half-reactions gives the overall reaction:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + \cancel{2e^-}}$$
$$\mathrm{2\,Ag^+(aq) + \cancel{2e^-} \rightarrow 2\,Ag(s)}$$
$$\mathrm{Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)}$$

This final equation is now balanced for both atoms and charge. The number of electrons gained and lost is equal, a requirement of redox reactions.

While simple redox reactions can often be balanced by inspection or trial and error, more complex reactions require a more systematic approach. The half-reaction method allows us to balance redox equations by separately balancing the oxidation and reduction processes, ensuring that both atoms and charge are conserved.

Balancing Redox Reactions Using the Half-Reaction Method

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $\mathrm{H^+(aq)}$ and $\mathrm{OH^-(aq)}$, as reactants or products. These equations can be challenging to balance by inspection, so a systematic approach called the half-reaction method is useful.

Balancing REDOX reactions via the half-reaction Method

This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding $\mathrm{H_2O}$.
4. Balance each half-reaction for H by adding $\mathrm{H^+}$.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons gained from one half-reaction equals the number of electrons lost from the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in basic solution, add $\mathrm{OH^-}$ ions to both sides to neutralize the $\mathrm{H^+}$ ions, then simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

Example 11.2.3: Balancing Equations for Redox Reactions in Acidic Solutions

Balance the following redox reaction, which occurs in acidic solution:

$$\mathrm{Cu(s) + HNO_3(aq) \rightarrow Cu^{2+}(aq) + NO(g)}$$

Solution

Identify which species are oxidized (oxidation number increases) and which are reduced (oxidation number decreases). This helps identify the species undergoing oxidation and reduction, which guides the half-reaction setup.

$$\mathrm{\overset{0}{Cu}(s) + \overset{+1+5-2}{HNO_3}(aq) \rightarrow Cu^{2+}(aq) + \overset{+2-2}{NO}(g)}$$

Cu: 0 to +2 ⇒ oxidized

N: +5 to +2 ⇒ reduced

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu(s) \rightarrow Cu^{2+}(aq)} \\ &\text{reduction:} && \mathrm{HNO_3(aq) \rightarrow NO(g)} \end{aligned}$$

Step 2: Balance each half-reaction for all elements except H and O. **Complete!**

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} \\ \text{reduction:}\quad & \mathrm{HNO_3(aq)} \rightarrow \mathrm{NO(g)}\end{aligned}$$

Step 3: Balance each half-reaction for $\mathbf{O}$ by adding $\mathbf{H2O}$:

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} \\ \text{reduction:}\quad & \mathrm{HNO_3(aq)} \rightarrow \mathrm{NO(g)} + \mathbf{2H2O(l)}\end{aligned}$$

Step 4: Balance each half-reaction for $\mathbf{H}$ by adding $\mathbf{H^+}$:

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} \\ \text{reduction:}\quad & \mathbf{3H^+(aq)} + \mathrm{HNO_3(aq)} \rightarrow \mathrm{NO(g)} + 2\,\mathrm{H_2O(l)}\end{aligned}$$

Step 5: Balance each half-reaction for **charge** by adding **electrons:**

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + \mathbf{2e^-} \\ \text{reduction:}\quad & \mathbf{3e^-} + 3\,\mathrm{H^+(aq)} + \mathrm{HNO_3(aq)} \rightarrow \mathrm{NO(g)} + 2\,\mathrm{H_2O(l)}\end{aligned}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons gained equals the number lost:

$$\begin{aligned}\text{oxidation } (\times 3):\quad & \mathbf{3}\ \mathrm{Cu(s)} \rightarrow \mathbf{3}\ \mathrm{Cu^{2+}(aq)} + \mathbf{6}\ \cancel{\mathbf{2}}\ \mathrm{e^-} \\ \text{reduction } (\times 2):\quad & \mathbf{6}\ \cancel{\mathbf{3}}\ \mathrm{e^-} + \mathbf{6}\ \cancel{\mathbf{3}}\ \mathrm{H^+(aq)} + \mathbf{2}\ \mathrm{HNO_3(aq)} \rightarrow \mathbf{2}\ \mathrm{NO(g)} + \mathbf{4}\ \cancel{\mathbf{2}}\ \mathrm{H_2O(l)}\end{aligned}$$

Step 7: Add the two half-reactions and simplify:

$$\begin{aligned}3\,\mathrm{Cu(s)} + \cancel{6e^-} + 6\,\mathrm{H^+(aq)} + 2\,\mathrm{HNO_3(aq)} &\rightarrow 3\,\mathrm{Cu^{2+}(aq)} + \cancel{6e^-} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)} \\ 3\,\mathrm{Cu(s)} + 6\,\mathrm{H^+(aq)} + 2\,\mathrm{HNO_3(aq)} &\rightarrow 3\,\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}\end{aligned}$$

Step 8: If the reaction takes place in basic solution, add $\mathrm{OH^-}$ ions to both sides to neutralize the $\mathrm{H^+}$ ions, then simplify.

This step is not necessary because the solution is acidic.

The balanced equation for the reaction in an acidic solution is then

$$3\,\mathrm{Cu(s)} + 6\,\mathrm{H^+(aq)} + 2\,\mathrm{HNO_3(aq)} \rightarrow 3\,\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$

A good final check is to verify that both atom counts and total charge are balanced:

Element	Reactants	Products
Cu	3	3
H	8	8
N	2	2
O	6	6

Total Charge

- Reactants: $3 \times 0\ (\mathrm{Cu}) + 6 \times (+1)\ (\mathrm{H^+}) + 2 \times 0\ (\mathrm{HNO_3}) = +6$
- Products: $3 \times (+2)\ (\mathrm{Cu^{2+}}) + 2 \times 0\ (\mathrm{NO}) + 4 \times 0\ (\mathrm{H_2O}) = +6$

Both atoms and total charge are balanced.

Exercise 11.2.3

Balance the following redox reaction, which occurs in acidic solution:

$$\mathrm{Cu\,(s) + 2\,H^+\,(aq) + 2\,HNO_3\,(aq) \rightarrow Cu^{2+}\,(aq) + 2\,NO_2\,(g) + 2\,H_2O\,(l)}$$

Answer available at the end of this section.

Example 11.2.4: Balancing Equations for Redox Reactions in Basic Solutions

Balance the following redox reaction, which occurs in basic solution:

$$\mathrm{Cr(OH)_3\,(s) + MnO_4^-\,(aq) \rightarrow CrO_4^{2-}\,(aq) + MnO_2\,(s)}$$

Solution

$$\mathrm{\overset{+3}{Cr}(\overset{-2}{O}\overset{+1}{H})_3\,(s) + \overset{+7}{Mn}\overset{-2}{O_4}^-\,(aq) \rightarrow \overset{+6}{Cr}\overset{-2}{O_4}^{2-}\,(aq) + \overset{+4}{Mn}\overset{-2}{O_2}\,(s)}$$

Cr: +3 to +6 ⇒ oxidized
Mn: +7 to +4 ⇒ reduced

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{Cr(OH)_3\,(s) \rightarrow CrO_4^{2-}\,(aq)}\\ \text{reduction:}\quad & \mathrm{MnO_4^-\,(aq) \rightarrow MnO_2\,(s)}\end{aligned}$$

Step 2: Balance each half-reaction for all elements except H and O. **Complete!**

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{Cr(OH)_3\,(s) \rightarrow CrO_4^{2-}\,(aq)}\\ \text{reduction:}\quad & \mathrm{MnO_4^-\,(aq) \rightarrow MnO_2\,(s)}\end{aligned}$$

Step 3: Balance each half-reaction for O by adding $\mathbf{H2O}$.

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{\mathbf{H2O(l)} + Cr(OH)_3\,(s) \rightarrow CrO_4^{2-}\,(aq)}\\ \text{reduction:}\quad & \mathrm{MnO_4^-\,(aq) \rightarrow MnO_2\,(s) + \mathbf{2H2O(l)}}\end{aligned}$$

Step 4: Balance each half-reaction for H by adding $\mathbf{H^+}$.

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{H_2O\,(l) + Cr(OH)_3\,(s) \rightarrow CrO_4^{2-}\,(aq) + \mathbf{5H^+(aq)}}\\ \text{reduction:}\quad & \mathrm{\mathbf{4H^+(aq)} + MnO_4^-\,(aq) \rightarrow MnO_2\,(s) + 2\,H_2O\,(l)}\end{aligned}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\begin{aligned}\text{oxidation:}\quad & \mathrm{H_2O\,(l) + Cr(OH)_3\,(s) \rightarrow CrO_4^{2-}\,(aq) + 5\,H^+\,(aq) + \mathbf{3e^-}}\\ \text{reduction:}\quad & \mathrm{\mathbf{3e^-} + 4\,H^+\,(aq) + MnO_4^-\,(aq) \rightarrow MnO_2\,(s) + 2\,H_2O\,(l)}\end{aligned}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons gained equals the number lost.

This step is not necessary since 3 electrons are lost and gained.

Step 7: Add the two half-reactions and simplify.

$$\cancel{H_2O\,(l)} + Cr(OH)_3\,(s) \rightarrow CrO_4{}^{2-}\,(aq) + \cancel{3}^{1}H^+\,(aq) + \cancel{3e^-}$$

$$+ \quad \cancel{3e^-} + \cancel{4\,H^+\,(aq)} + MnO_4{}^-\,(aq) \rightarrow MnO_2\,(s) + \cancel{2}^{1}\,H_2O\,(l)$$

$$Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \rightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + H^+\,(aq) + H_2O\,(l)$$

Step 8: If the reaction takes place in basic solution, add OH^- ions to both sides to neutralize the H^+ ions, then simplify.

$$OH^-\,(aq) + Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \rightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + \cancel{H^+\,(aq)} + H_2O\,(l) + \cancel{OH^-\,(aq)}$$

$H^+ + OH^- \rightarrow H_2O\,(l)$ giving the balanced equation in basic solution:

$$OH^-\,(aq) + Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \rightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + 2\,H_2O\,(l)$$

Final Check

Element	Reactants	Products
Cr	1	1
O	8	8
H	4	4
Mn	1	1

Total Charge:

- Reactants: -1 + 0 + -1 = -2
- Products: -2 + 0 + 0 = -2

Both atoms and total charge are balanced.

Exercise 11.2.4

Balance the following redox reaction, which occurs in basic solution:

$$MnO_4{}^-\,(aq) + Br^-\,(aq) \rightarrow MnO_2\,(s) + BrO_3{}^-\,(aq)$$

Answer available at the end of this section.

Summary

Redox (reduction–oxidation) reactions involve the transfer of electrons between species. In these reactions, one substance is oxidized (loses electrons) and another is reduced (gains electrons). Oxidation numbers are a helpful tool for identifying which atoms are oxidized or reduced and for determining whether a reaction is a redox process.

To balance redox reactions, especially in aqueous solutions, the half-reaction method provides a systematic approach that ensures both atoms and charges are conserved. This method involves balancing atoms other than hydrogen and oxygen, then oxygen with water, hydrogen with H^+ (or OH^- in basic solutions), and finally balancing charge by adding electrons.

Glossary

electrochemistry
: The study of the relationship between chemical reactions and electron flow.

half-reaction method
: A method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation

"half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction.

oxidation
The process in which a species loses electrons.

oxidation half-reaction
The "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced.

oxidation number
A tool to keep track of electron transfer during redox reactions, increasing upon oxidation and decreasing upon reduction; also called oxidation state.

oxidation-reduction reaction
A broad type of reaction where one substance loses electrons through oxidation and another gains electrons through reduction; also called a redox reaction

oxidizing agent
The species that accepts electrons from the other reactant and is itself reduced.

reducing agent
The species that provides electrons to the other reactant and is itself oxidized.

reduction
The process in which a species gains electrons.

reduction half-reaction
The "half" of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced.

Answers

Exercise 11.2.1

a) K is +1 (Group 1 element)
O is -2
Let x = oxidation number of Cl:
(+1) + x + 3(-2) = 0 ⇒ x = +5
Cl is +5.
Note: Although chlorine often has an oxidation number of –1, in this compound it is bonded to more electronegative oxygen atoms, resulting in a positive oxidation number.

b) O is -2
Let x = oxidation number of S:
x + 4(-2) = -2 ⇒ x = +6.
S is +6.

Exercise 11.2.2

a) $\overset{0}{\mathrm{Cu}}(\mathrm{s}) + 2\mathrm{Ag}^{\overset{+1}{+}}(\mathrm{aq}) \rightarrow \mathrm{Cu}^{\overset{+2}{2+}}(\mathrm{aq}) + 2\overset{0}{\mathrm{Ag}}(\mathrm{s})$
Cu: oxidation number goes from 0 to +2 → oxidized, reducing agent
Ag: oxidation number goes from +1 to 0 → reduced, oxidizing agent

b) $\overset{+2\,-1}{\mathrm{FeCl_2}}(\mathrm{aq}) + 2\,\overset{+1\,-2+1}{\mathrm{NaOH}}(\mathrm{aq}) \rightarrow \overset{+2\,-2+1}{\mathrm{Fe(OH)_2}}(\mathrm{s}) + 2\,\overset{+1\,-1}{\mathrm{NaCl}}(\mathrm{aq})$
Not a redox reaction. All atoms retain the same oxidation numbers.

c) $\overset{0}{\mathrm{Zn}}(\mathrm{s}) + 2\,\overset{+1-1}{\mathrm{HCl}}(\mathrm{aq}) \rightarrow \overset{+2\,-1}{\mathrm{ZnCl_2}}(\mathrm{aq}) + \overset{0}{\mathrm{H_2}}(\mathrm{g})$
Zn: oxidation number goes from 0 to +2 → oxidized, reducing agent
H: oxidation number goes from +1 to 0 → reduced, oxidizing agent

Exercise 11.2.3

$$\overset{0}{\mathrm{Cu}}(\mathrm{s}) + 2\,\overset{+1+5-2}{\mathrm{HNO_3}}(\mathrm{aq}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq}) + 2\,\overset{+4-2}{\mathrm{NO_2}}(\mathrm{g}) + 2\,\mathrm{H_2O}(\mathrm{l})$$

Cu: 0 to +2 ⇒ oxidized
N: +5 to +4 ⇒ reduced
Step 1: Write skeletal half-reactions.

- Oxidation: $\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)}$
- Reduction: $\mathrm{HNO_3(aq)} \rightarrow \mathrm{NO_2(g)}$

Step 2: Balance each half-reaction for all elements except H and O. **Complete!**

Step 3: Balance O atoms by adding $\mathrm{H_2O}$.

$\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)}$

$\mathrm{HNO_3(aq)} \rightarrow \mathrm{NO_2(g)} + \mathbf{H2O(l)}$

Step 4: Balance H atoms by adding $\mathrm{H^+}$.

$\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)}$

$\mathbf{H^+} + \mathrm{HNO_3(aq)} \rightarrow \mathrm{NO_2(g)} + \mathrm{H_2O(l)}$

Step 5: Balance charges by adding electrons.

- Oxidation: $\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + \mathbf{2}\,\mathrm{e^-}$
- Reduction: $\mathbf{e^-} + \mathrm{H^+} + \mathrm{HNO_3(aq)} \rightarrow \mathrm{NO_2(g)} + \mathrm{H_2O(l)}$

Step 6: Multiply half-reactions to equalize electrons.

- Oxidation (×1): $\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-}$
- Reduction (×2): $\mathbf{2}\mathrm{e^-} + \mathbf{2}\mathrm{H^+} + \mathbf{2}\mathrm{HNO_3(aq)} \rightarrow \mathbf{2}\mathrm{NO_2(g)} + \mathbf{2}\mathrm{H_2O(l)}$

Step 7: Add the half-reactions and simplify.

$$\mathrm{Cu(s)} + \cancel{2e^-} + 2\,\mathrm{H^+} + 2\,\mathrm{HNO_3(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + \cancel{2e^-} + 2\,\mathrm{NO_2(g)} + 2\,\mathrm{H_2O(l)}$$
$$\mathrm{Cu(s)} + 2\,\mathrm{H^+} + 2\,\mathrm{HNO_3(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{NO_2(g)} + 2\,\mathrm{H_2O(l)}$$

Step 8: This reaction occurs in acidic solution, so no adjustment for $\mathrm{OH^-}$ is needed.

Final Check

Element	Reactants	Products
Cu	1	1
H	4	4
N	2	2
O	6	6

Total Charge:

- Reactants: $1 \times 0 + 2 \times (+1) + 2 \times 0 = +2$
- Products: $1 \times (+2) + 2 \times 0 + 2 \times 0 = +2$

Both atoms and total charge are balanced.

Exercise 11.2.4

$$\overset{+7}{\mathrm{Mn}}\overset{-2}{\mathrm{O_4}}^-\mathrm{(aq)} + \overset{-1}{\mathrm{Br}}^-\mathrm{(aq)} \rightarrow \overset{+4}{\mathrm{Mn}}\overset{-2}{\mathrm{O_2}}\mathrm{(s)} + \overset{+5}{\mathrm{Br}}\overset{-2}{\mathrm{O_3}}^-\mathrm{(aq)}$$

Br: -1 to +5 ⇒ oxidized
Mn: +7 to +4 ⇒ reduced

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad \mathrm{Br^-(aq)} \rightarrow \mathrm{BrO_3^-(aq)}$$
$$\text{reduction:} \quad \mathrm{MnO_4^-(aq)} \rightarrow \mathrm{MnO_2(s)}$$

Step 2: Balance each half-reaction for all elements except H and O.

Mn and Br are already balanced.

Step 3: Balance each half-reaction for O by adding $\mathbf{H2O}$.

$$\text{oxidation:} \quad \mathbf{3H2O(l)} + \mathrm{Br^-(aq)} \rightarrow \mathrm{BrO_3^-(aq)}$$
$$\text{reduction:} \quad \mathrm{MnO_4^-(aq)} \rightarrow \mathrm{MnO_2(s)} + \mathbf{2H2O(l)}$$

Step 4: Balance each half-reaction for H by adding $\mathbf{H^+}$.

$$\text{oxidation:} \quad \mathrm{3\,H_2O(l)} + \mathrm{Br^-(aq)} \rightarrow \mathrm{BrO_3^-(aq)} + \mathbf{6H^+(aq)}$$
$$\text{reduction:} \quad \mathbf{4H^+(aq)} + \mathrm{MnO_4^-(aq)} \rightarrow \mathrm{MnO_2(s)} + \mathrm{2\,H_2O(l)}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad \mathrm{3\,H_2O(l)} + \mathrm{Br^-(aq)} \rightarrow \mathrm{BrO_3^-(aq)} + \mathrm{6\,H^+(aq)} + \mathbf{6e^-}$$
$$\text{reduction:} \quad \mathbf{3e^-} + \mathrm{4\,H^+(aq)} + \mathrm{MnO_4^-(aq)} \rightarrow \mathrm{MnO_2(s)} + \mathrm{2\,H_2O(l)}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons gained equals the number lost.

$$\text{oxidation:} \quad \mathrm{3\,H_2O(l)} + \mathrm{Br^-(aq)} \rightarrow \mathrm{BrO_3^-(aq)} + \mathrm{6\,H^+(aq)} + \mathrm{6\,e^-}$$
$$\text{reduction:} \quad \mathbf{6}\,\mathrm{e^-} + \mathbf{8}\mathrm{H^+(aq)} + \mathbf{2}\mathrm{MnO_4^-(aq)} \rightarrow \mathbf{2}\mathrm{MnO_2(s)} + \mathbf{4}\,\mathrm{H_2O(l)}$$

Step 7: Add the two half-reactions and simplify.

$$\cancel{3\,H_2O\,(l)} + Br^-\,(aq) \rightarrow BrO_3{}^-\,(aq) + \cancel{6\,H^+\,(aq)} + \cancel{6\,e^-}$$

$$+ \quad \cancel{6\,e^-} + \cancel{8}^{2}\,H^+\,(aq) + 2\,MnO_4{}^-\,(aq) \rightarrow 2\,MnO_2\,(s) + \cancel{4}^{1}\,H_2O\,(l)$$

$$Br^-\,(aq) + 2\,H^+\,(aq) + 2\,MnO_4{}^-\,(aq) \rightarrow BrO_3{}^-\,(aq) + 2\,MnO_2\,(s) + H_2O\,(l)$$

Step 8: If the reaction takes place in basic solution, add OH^- ions to both sides to neutralize the H^+ ions, then simplify.

$$Br^-\,(aq) + 2\,H^+\,(aq) + \mathbf{2OH^-} + 2\,MnO_4{}^-\,(aq) \rightarrow BrO_3{}^-\,(aq) + 2\,MnO_2\,(s) + H_2O\,(l) + \mathbf{2OH^-}$$

$H^+ + OH^- \rightarrow H_2O\,(l)$ giving the balanced equation in basic solution:

$$Br^-\,(aq) + \cancel{2}^{1}\,H_2O\,(l) + 2\,MnO_4{}^-\,(aq) \rightarrow BrO_3{}^-\,(aq) + 2\,MnO_2\,(s) + \cancel{H_2O\,(l)} + 2\,OH^-\,(aq)$$

$$Br^-\,(aq) + H_2O\,(l) + 2\,MnO_4{}^-\,(aq) \rightarrow BrO_3{}^-\,(aq) + 2\,MnO_2\,(s) + 2\,OH^-\,(aq)$$

Final Check

Element	Reactants	Products
Br	1	1
O	9	9
H	2	2
Mn	2	2

Total Charge:

Reactants: -1 + 0 + 2(-1) = -3 Products: -1 + 0 + 2(-1) = -3

Both atoms and total charge are balanced.

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11.3: Galvanic Cells

Learning Objectives

- Identify the components of a galvanic cell and their roles in converting chemical energy to electrical energy.
- Write balanced half-reactions and the overall reaction for a galvanic cell.
- Use shorthand (cell) notation to represent a galvanic cell.

Galvanic cells, also called voltaic cells, are devices that turn chemical energy into electrical energy using spontaneous redox reactions. These cells power everyday items like batteries and help us understand how chemical reactions can produce useful electricity. To see how this works, we often separate the overall redox reaction into two half-reactions: one for oxidation and one for reduction. This makes it easier to balance the equations and see which chemical species are gaining or losing electrons during the process.

Before we look at how a galvanic cell works, let's first see what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure 11.3.1). As soon as the copper metal is added, silver metal begins to form on the copper surface while copper ions pass into the solution. The blue colour of the solution (on the far right) indicates the presence of copper ions.

We can better understand what is happening by splitting the reaction into its two half-reactions:

$$\begin{aligned} &\text{oxidation: } \mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-} \\ &\text{reduction: } 2 \times (\mathrm{Ag^+(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}) \qquad \text{or} \qquad 2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Ag(s)} \\ &\text{overall: } 2\,\mathrm{Ag^+(aq)} + \mathrm{Cu(s)} \rightarrow 2\,\mathrm{Ag(s)} + \mathrm{Cu^{2+}(aq)} \end{aligned}$$

Notice that the reduction half-reaction is multiplied by two so that the number of electrons gained in the reduction equals the number of electrons lost in the oxidation.

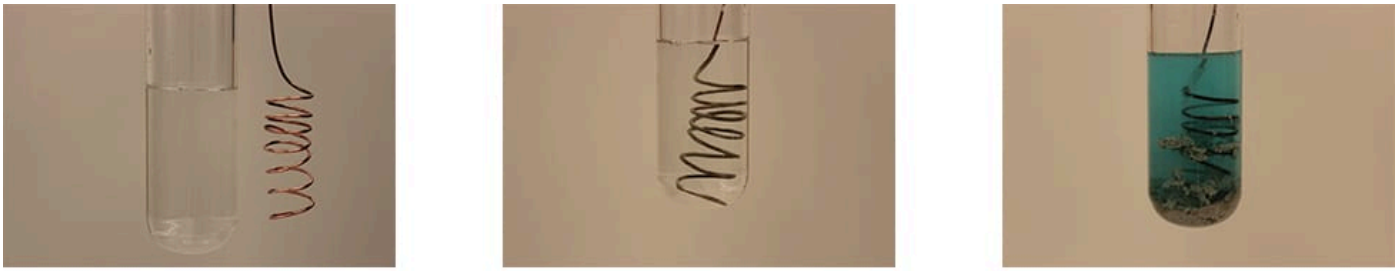


Figure 11.3.1: When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs, exchanging $\mathrm{Cu^{2+}}$ for $\mathrm{Ag^+}$ in solution. As the reaction proceeds (b), silver metal is deposited on the copper strip while the solution turns blue (c) as silver ions in the solution are replaced by copper ions. (credit: modification of work by Mark Ott)

Galvanic Cells

In the previous example, we saw that when a copper wire is placed directly into a silver nitrate solution, a redox reaction occurs spontaneously, with silver metal forming on the copper while copper ions enter the solution. However, in that setup, the energy from the electron transfer is released to the surroundings rather than being captured as usable electrical energy.

To harness that energy to do work, we can set up a galvanic (or voltaic) cell, which uses the same spontaneous redox reaction but separates the oxidation and reduction half-reactions into different containers (Figure 11.3.2). This separation allows electrons to flow through an external wire, generating an electric current that can power a device or be measured.

In this setup, the left beaker is a half-cell containing a 1 M solution of copper(II) nitrate ($\mathrm{Cu(NO_3)_2}$) with a copper metal electrode. Here, copper undergoes oxidation and releases electrons, so the copper electrode is the anode.

The right beaker is another half-cell containing a 1 M solution of silver nitrate ($\mathrm{AgNO_3}$) with a silver electrode. Here, silver ions in the solution gain electrons and are reduced to silver metal, making the silver electrode the cathode.

The reaction that occurs is the same as in the earlier example:

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2\,e^-}\\&\underline{\text{cathode (reduction): } \mathrm{2\,Ag^+\,(aq) + 2\,e^- \rightarrow 2\,Ag\,(s)}}\\&\text{overall: } \mathrm{2\,Ag^+\,(aq) + Cu\,(s) \rightarrow 2\,Ag\,(s) + Cu^{2+}\,(aq)}\end{aligned}$$

Electrons released during oxidation at the anode give it a negative charge, while the cathode, which attracts these electrons, carries a positive charge. This charge difference creates a potential difference that drives electron flow through the external circuit.

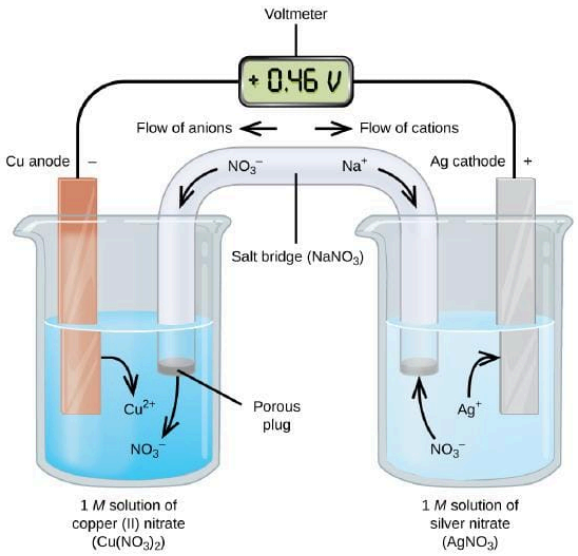


Figure 11.3.2: In this standard galvanic cell, the oxidation and reduction half-reactions are separated into different half-cells, allowing electrons to flow through an external wire and do electrical work.

The two electrodes are connected by wires through a voltmeter to measure the voltage. However, until the salt bridge is in place, no current flows because the circuit is incomplete. To complete the circuit and allow ions to move between the half-cells to maintain electrical neutrality, we use a salt bridge containing a concentrated, nonreactive electrolyte solution (such as sodium nitrate, $\mathrm{NaNO_3}$).

As the reaction proceeds:

- Electrons flow from the copper anode to the silver cathode through the wire.
- Nitrate ions ($\mathrm{NO_3^-}$) move into the copper solution to balance the positive charge from the $\mathrm{Cu^{2+}}$ formed during oxidation.
- Sodium ions ($\mathrm{Na^+}$) move into the silver solution to replace the $\mathrm{Ag^+}$ ions being reduced and deposited as silver metal.

In addition to completing the circuit, the salt bridge prevents charge buildup, which would otherwise stop the flow of electrons.

When the circuit is completed, the voltmeter shows a positive voltage, known as the cell potential. This voltage is a measure of the electrical potential difference between the two electrodes and indicates how much energy per unit charge can be obtained from the redox reaction. For this copper–silver cell under standard conditions, the cell potential is +0.46 V, which confirms that the redox reaction is spontaneous and can produce electrical energy. The next section will explore how to calculate and interpret cell potentials.

Note

Oxidation always occurs at the anode (**AN OX** – vowels go together!).

Reduction always occurs at the cathode (**RED CAT** – consonants go together!).

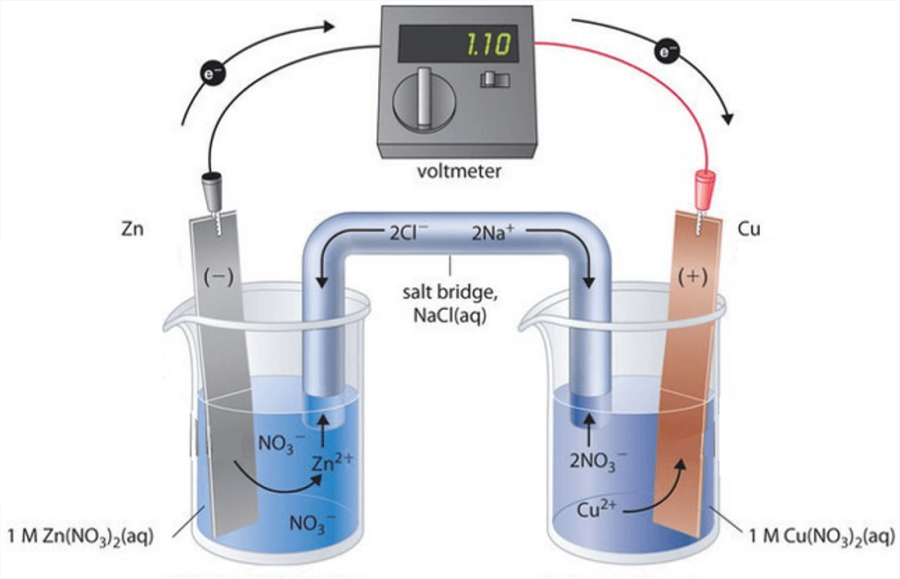
Electrons flow from the anode to the cathode in a galvanic cell.





Example 11.3.1

A galvanic cell is constructed of a $\mathrm{Zn/Zn^{2+}}$ half cell and a $\mathrm{Cu/Cu^{2+}}$ half cell:



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Electrons flow from the zinc electrode to the copper electrode.

a) Write the half-reactions for each half-cell.

b) Which electrode is the anode and which is the cathode?

c) Over time what will happen to the mass of the Zn electrode? The Cu electrode? Explain your reasoning.

d) Rationalize the flow of ions in the salt-bridge. Why is this necessary for the cell to continue operating?

Solution

a) Electrons flow from the zinc electrode to the copper electrode.

Oxidation is the process of losing electrons.

Since the zinc electrode is the source of the electrons flowing through the external circuit, it must be losing electrons.

Therefore, oxidation occurs at the zinc electrode:

$\mathrm{Zn\,(s)\ \rightarrow Zn^{2+}\,(aq) + 2\,e^-}$

Conversely:

Reduction is the process of gaining electrons.

The copper electrode is receiving electrons coming through the wire from the zinc electrode.

Therefore, reduction occurs at the copper electrode:

$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$

b)Anode: The Zn electrode is the anode because oxidation occurs here (loss of electrons).

Cathode: The Cu electrode is the cathode because reduction occurs here (gain of electrons).

c) Mass Changes Over Time:

At the Zn anode, zinc metal is oxidized to $\mathrm{Zn^{2+}}$, which enters the solution, so the mass of the Zn electrode decreases over time.

At the Cu cathode, $\mathrm{Cu^{2+}}$ ions in solution are reduced to solid Cu, which plates onto the electrode, so the mass of the Cu electrode increases over time.

Click for image of electrodes available at the end of this section.

d)The salt bridge allows ions to move to maintain charge neutrality:

At the anode (Zn):

As $\mathrm{Zn^{2+}}$ ions enter the solution, the solution becomes more positively charged.

Anions ($\mathrm{Cl^-}$) from the salt bridge move toward the anode to balance the charge.

At the cathode (Cu):

As $\mathrm{Cu^{2+}}$ ions are removed from solution, the solution becomes more negatively charged.

Cations ($\mathrm{Na^+}$) from the salt bridge move toward the cathode to balance the charge.

Without this ion flow, charge would build up in each half-cell, preventing further electron flow and stopping the cell from functioning.

Exercise 11.3.1

A galvanic cell is constructed with a magnesium electrode in a $\mathrm{Mg^{2+}}$ solution and a silver electrode in a $\mathrm{Ag^+}$ solution. Electrons flow from the magnesium electrode to the silver electrode.

a) Write the half-reactions for the oxidation and reduction occurring in this cell.

b) What is the overall reaction occurring in the galvanic cell?

c) Identify which electrode is the anode and which is the cathode.

Answer available at the end of this section.

Chemistry in Everyday Life: Single Use Batteries

A common single use battery is the dry cell (Figure 11.3.3), which uses a zinc can as both container and anode (– terminal) and a graphite rod as the cathode (+ terminal). The Zn can is filled with an electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water. As the battery operates:

At the anode, zinc is oxidized:

$$\mathrm{Zn\,(s)} \rightarrow \mathrm{Zn^{2+}\,(aq)} + 2\,\mathrm{e^-}$$

At the cathode, manganese(IV) oxide is reduced:

$$2\,\mathrm{MnO_2\,(s)} + 2\,\mathrm{NH_4Cl\,(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{Cl^-}$$

Giving the overall reaction:

$$2\,\mathrm{MnO_2\,(s)} + 2\,\mathrm{NH_4Cl\,(aq)} + \mathrm{Zn\,(s)} \rightarrow \mathrm{Zn^{2+}\,(aq)} + \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{Cl^-}$$

Dry cells produce about 1.5 V. They come in various sizes (D, C, AA, AAA), but the voltage remains the same regardless of size. Larger cells simply contain more reactants, allowing them to power devices longer. Multiple dry cells can be connected in series in devices (like flashlights) to produce higher voltages.

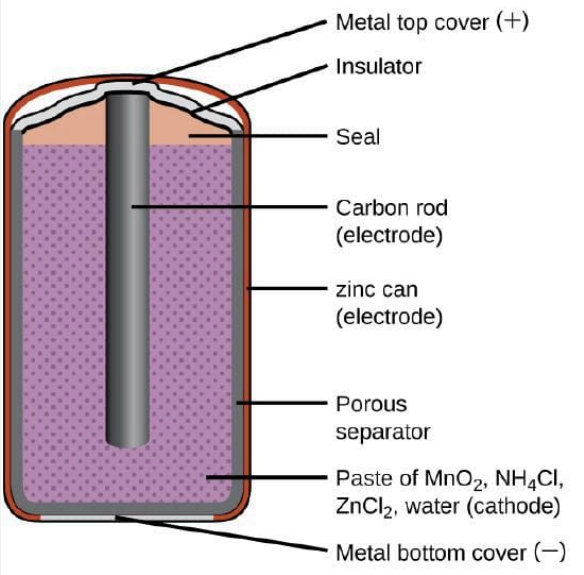


Figure 11.3.3: Cross-section of a typical dry cell battery.

Alkaline batteries (Figure 11.3.4) were developed in the 1950s as improved dry cells. They use the same redox couples but replace the acidic paste with an alkaline potassium hydroxide electrolyte, which increases efficiency and extends the battery's lifespan.

The cell reactions are:

anode: $\mathrm{Zn\,(s)} + 2\,\mathrm{OH^-\,(aq)} \rightarrow \mathrm{ZnO\,(s)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{e^-}$

cathode: $2\,\mathrm{MnO_2\,(s)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{OH^-\,(aq)}$

overall: $\mathrm{Zn\,(s)} + 2\,\mathrm{MnO_2\,(s)} \rightarrow \mathrm{ZnO\,(s)} + \mathrm{Mn_2O_3\,(s)} \qquad E_{\mathrm{cell}} = +1.43\ \mathrm{V}$

Alkaline batteries can deliver three to five times more energy than zinc-carbon dry cells of the same size, making them longer-lasting in devices like remotes, clocks, and flashlights. However, they can leak potassium hydroxide if left in devices for extended periods. Most alkaline batteries are not rechargeable, and attempting to recharge them can cause rupture and leakage.

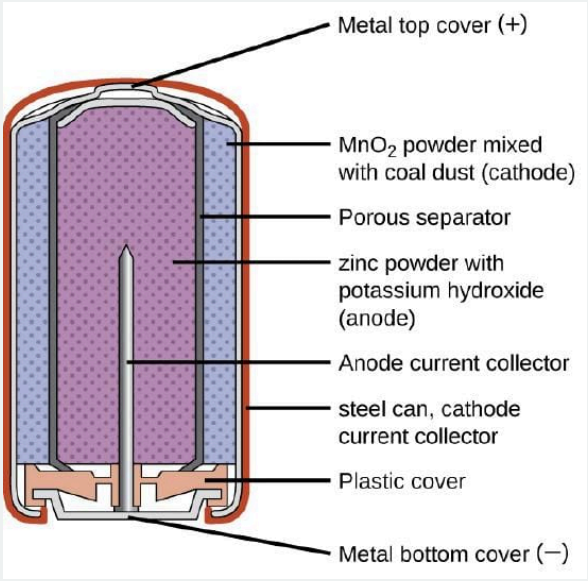


Figure 11.3.4: Cross-section of an alkaline battery, which was developed as an improved replacement for zinc-carbon (dry cell) batteries, providing longer life and higher energy output.

Dry cells and alkaline batteries are practical examples of galvanic cells, converting chemical energy directly into electrical energy. They allow us to carry portable electricity in our backpacks, pockets, and devices, and understanding their chemistry connects the everyday act of replacing batteries to the redox reactions you learn in this course.

Shorthand Notation for Galvanic Cells

Describing galvanic cells in words or diagrams each time can be inconvenient, especially since there are many possible galvanic cells we might encounter in chemistry. To address this, chemists use a standardized shorthand notation (sometimes called a cell diagram) to represent galvanic cells clearly and efficiently. This notation concisely shows the species involved in the redox reaction, the direction of electron flow, and the operating conditions of the cell.

In this notation, the anode is written on the left, followed by the anode solution, the salt bridge (‖), the cathode solution, and finally the cathode on the right. Within each half-cell, species generally appear in the order they participate in the half-reaction (reactants then products), with electrodes placed on the outside.

- A vertical line, $|$, denotes a phase boundary (for example, between a solid electrode and an aqueous solution).
- A double vertical line, ‖, denotes the salt bridge (or porous barrier) separating the half-cells.
- Spectator ions are not included, and the simplest form of each half-reaction is used.
- Initial concentrations of the ions are often included when known.

Figure 11.3.5 shows the shorthand notation from the $\mathrm{Zn/Cu^{2+}}$ galvanic cell shown in Example 11.3.1.

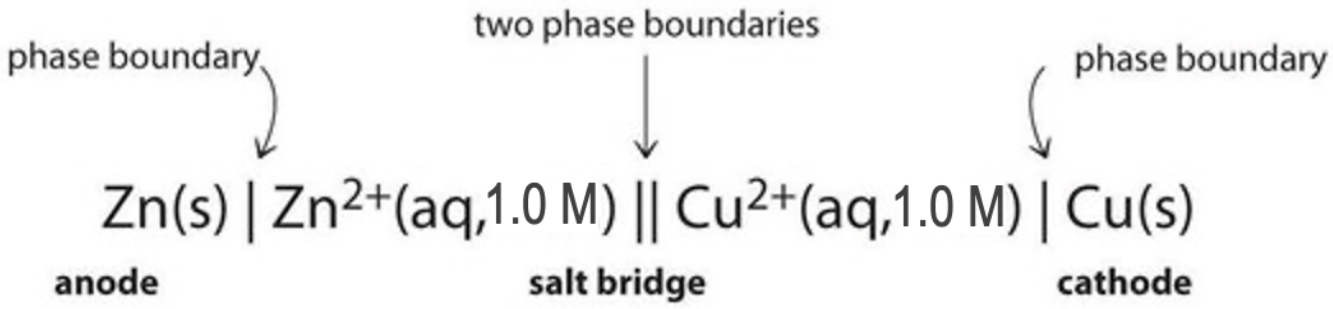
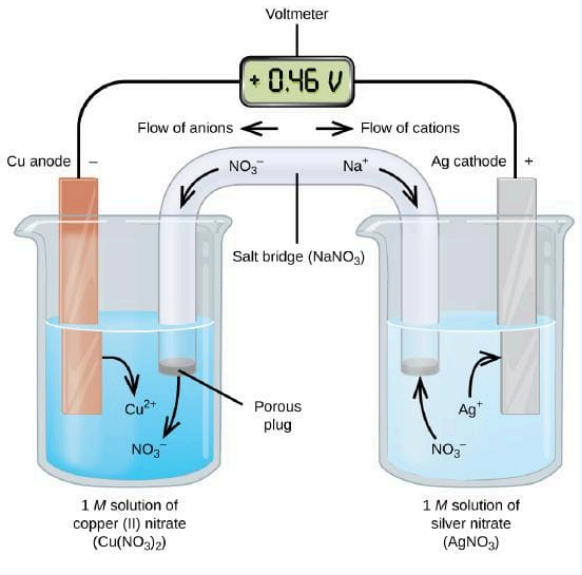


Figure 11.3.5: Shorthand notation for a $\mathrm{Zn/Cu^{2+}}$ galvanic cell. The anode species are on the left, the cathode species on the right, with the salt bridge (‖) in the middle. The concentrations of aqueous ions are included in parentheses (1 M under standard conditions).

Exercise 11.3.2

Write the shorthand notation for the galvanic cell in Figure 11.3.2 and shown here:



Answer available at the end of this section.

Some oxidation-reduction reactions involve species that are poor electrical conductors, requiring the use of an electrode that does not participate in the reaction. Frequently, the electrode is platinum, gold, or graphite, all of which are inert in most chemical reactions.

One such system is shown in Figure 11.3.6. Magnesium undergoes oxidation at the anode on the left, while hydrogen ions undergo reduction at the cathode on the right:

$$\begin{aligned}&\text{oxidation: } \mathrm{Mg\,(s) \rightarrow Mg^{2+}\,(aq) + 2\,e^-}\\&\text{reduction: } \mathrm{2\,H^+\,(aq) + 2\,e^- \rightarrow H_2\,(g)}\\&\hline\\&\text{overall: } \mathrm{Mg\,(s) + 2\,H^+\,(aq) \rightarrow Mg^{2+}\,(aq) + H_2\,(g)}\end{aligned}$$

An inert platinum electrode is used as the cathode because the reduction half-reaction does not involve a solid product that can act as an electrode. In cell notation, the inert electrode is placed at the end of the cathode half-cell:

$$\mathrm{Mg\,(s)\,|\,Mg^{2+}\,(aq)\,\|\,H^{+}\,(aq)\,|\,H_2\,(g)\,|\,Pt\,(s)}$$

The magnesium electrode is an active electrode because it participates in the redox reaction, whereas the platinum electrode is inert; it does not participate in the reaction and serves only to conduct electrons and complete the circuit.

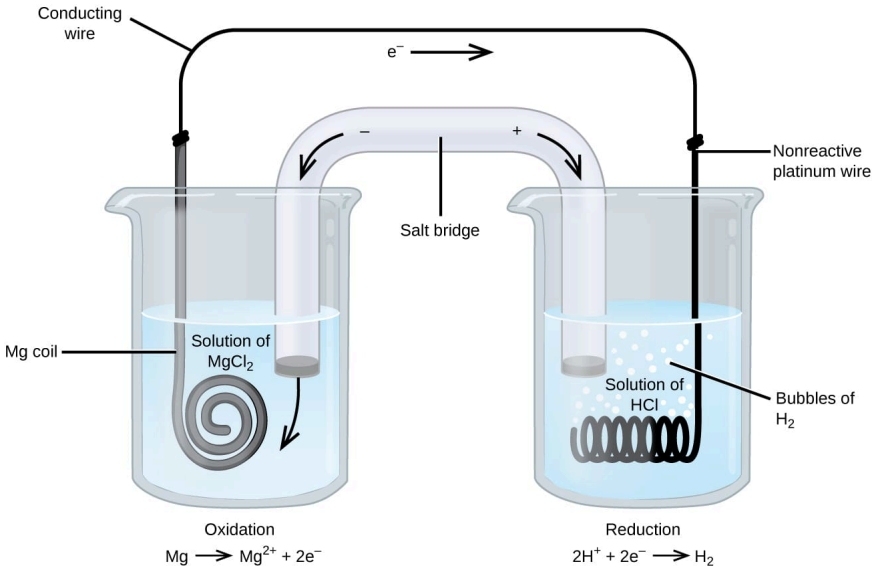


Figure 11.3.6: A galvanic cell for the oxidation of magnesium and the reduction of hydrogen ions, using an inert platinum electrode as the cathode.

Example 11.3.2: Using Cell Notation

The following overall reaction occurs in a galvanic cell:

$$\mathrm{2\,Cr(\mathit{s}) + 3\,Cu^{2+}\,(aq) \rightarrow 2\,Cr^{3+}\,(aq) + 3\,Cu(\mathit{s})}$$

Write the oxidation and reduction half-reactions, identify which occurs at the anode and at the cathode, and write the cell notation.

Solution

The half-reactions are:

$$\begin{aligned} \mathrm{2\,Cr\,(s)} &\rightarrow \mathrm{2\,Cr^{3+}\,(aq) + 6\,e^{-}} \\ \mathrm{3\,Cu^{2+}\,(aq) + 6\,e^{-}} &\rightarrow \mathrm{3\,Cu\,(s)} \\ \hline \mathrm{2\,Cr\,(s) + 3\,Cu^{2+}\,(aq)} &\rightarrow \mathrm{2\,Cr^{3+}\,(aq) + 3\,Cu\,(s)} \end{aligned}$$

Cr loses electrons, so the first reaction is the oxidation half-reaction and occurs at the anode.

$\mathrm{Cu^{2+}}$ gains electrons, so the bottom reaction is the reduction half-reaction and occurs at the cathode.

Cell notation uses the simplest form of each half-reaction and begins with the species at the anode. Since no concentrations are specified:

$$\mathrm{Cr\,(s)\,|\,Cr^{3+}\,(aq)\,\|\,Cu^{2+}\,(aq)\,|\,Cu\,(s)}$$

Exercise 11.3.3

The following overall reaction occurs in a galvanic cell with platinum electrodes:

$$5\,Fe^{2+}(aq) + MnO_4{}^-(aq) + 8\,H^+(aq) \rightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

Write the oxidation and reduction half-reactions, identify which occurs at the anode and at the cathode, and write the cell notation.

Answer available at the end of this section.

Summary

A galvanic cell (or voltaic cell) is an electrochemical cell that uses a spontaneous redox reaction to generate electrical energy. The cell separates the oxidation half-reaction from the reduction half-reaction, allowing the transfer of electrons to occur through an external wire so that the energy from the spontaneous reaction can do work.

Galvanic cells typically consist of two half-cells. One half-cell, usually shown on the left, contains the anode (negative), where oxidation occurs. The other half-cell, typically shown on the right, contains the cathode (positive), where reduction occurs.

A salt bridge is used to complete the circuit, allowing current to flow. Anions in the salt bridge flow toward the anode (to balance positive charge from oxidation), while cations flow toward the cathode (to replace the reduced ions). This movement maintains electrical neutrality in each half-cell and completes the circuit.

Galvanic cells can be described using cell notation. In this notation, information about the anode half-reaction appears on the left, and information about the cathode half-reaction appears on the right. The salt bridge is represented by a double vertical line, ||, and different phases within a half-cell are separated by a single vertical line, |.

Active electrodes participate in the redox reaction. Inert electrodes do not participate in the redox reaction but provide a surface for electron transfer, allowing current to flow. Inert electrodes are often made from platinum or gold, which are stable in many chemical environments.

Glossary

active electrode
: An electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction.

anode
: An electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation.

cathode
: An electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation.

cell notation
: Shorthand way to represent the reactions in an electrochemical cell.

galvanic cell
: An electrochemical cell that turns chemical energy into electrical energy using spontaneous redox reactions; also called a voltaic cell.

inert electrode
: An electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

salt bridge
: A galvanic cell component allowing ions to move between the half-cells to maintain electrical neutrality and preventing charge buildup.

voltmeter
: An instrument that measures electrical potential difference (voltage) between two electrodes in an electrochemical cell.

Answers

Example 11.3.1



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Exercise 11.3.1

a) Electrons flow from the magnesium electrode to the silver electrode, so:

Oxidation (at the anode):

$\mathrm{Mg(s)} \rightarrow \mathrm{Mg^{2+}(aq)} + 2\,\mathrm{e^-}$

Reduction (at the cathode):

$\mathrm{Ag^+(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}$

b) Since the oxidation half-reaction involves two electrons, we multiply the reduction half-reaction by 2 to balance electron transfer.

$2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Ag(s)}$

Overall reaction: $2\,\mathrm{Ag^+(aq)} + \mathrm{Mg(s)} \rightarrow \mathrm{Mg^{2+}(aq)} + 2\,\mathrm{Ag(s)}$

c) The magnesium electrode is the anode because oxidation occurs there (loss of electrons). The silver electrode is the cathode because reduction occurs there (gain of electrons).

Exercise 11.3.2

At the anode:

$\text{anode (oxidation)}\colon \mathrm{Cu}(s) \rightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-}$

This is written as:

$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}$

where | indicates the phase boundary between the copper electrode and $\mathrm{Cu^{2+}}$ ions in solution.

At the cathode:

$\text{cathode (reduction)}\colon 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Ag}(s)$

This is written as:

$\mathrm{Ag^+}\,|\,\mathrm{Ag}(s)$

Since the shorthand notation uses the simplest form of each half-reaction, we do not include the coefficient "2" in front of $\mathrm{Ag^+}$ and Ag.

The complete shorthand notation, with the salt bridge shown as ‖, is:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

Exercise 11.3.3

The half-reactions are:

$$\begin{gathered} 5\,\mathrm{Fe^{2+}(aq)} \rightarrow 5\,\mathrm{Fe^{3+}(aq)} + 5\,\mathrm{e^-} \\ \mathrm{MnO_4{}^-(aq)} + 8\mathrm{H^+(aq)} + 5\mathrm{e^-} \rightarrow \mathrm{Mn^{2+}(aq)} + 4\mathrm{H_2O(l)} \\ \hline 5\,\mathrm{Fe^{2+}(aq)} + \mathrm{MnO_4{}^-(aq)} + 8\mathrm{H^+(aq)} \rightarrow 5\,\mathrm{Fe^{3+}(aq)} + \mathrm{Mn^{2+}(aq)} + 4\mathrm{H_2O(l)} \end{gathered}$$

$\mathrm{Fe^{2+}}$ loses electrons, so the first reaction is the oxidation half-reaction and occurs at the anode.

In the second half-reaction, electrons are gained, so it is the reduction half-reaction and occurs at the cathode.

Cell notation uses the simplest form of each half-reaction and begins with the species at the anode. Since no concentrations are specified:

$$\mathrm{Pt\,(s)\,|\,Fe^{2+}\,(aq),\ Fe^{3+}\,(aq)\,\|\,MnO_4{}^{-}\,(aq),\ H^{+}\,(aq),\ Mn^{2+}\,(aq)\,|\,Pt\,(s)}$$

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11.4: Cell Potentials

Learning Objectives

- Use standard reduction potential tables to predict the direction of redox reactions, identify the anode and cathode in a galvanic cell, and calculate the standard cell potential (E°_{cell}).
- Interpret the sign of E°_{cell} in terms of spontaneity under standard conditions.
- Use standard reduction potential tables to compare the relative strength of oxidizing and reducing agents.

Cell Potentials

What drives a galvanic cell?

Consider the galvanic cell with the following overall reaction:

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq)\ \rightarrow Zn^{2+}\,(aq) + Cu\,(s)}$$

In this cell, a current is produced when electrons flow externally from the Zn anode to the Cu cathode, where $\mathrm{Cu^{2+}}$ is reduced. Why do electrons flow from zinc to copper in this cell?

We can think of the redox reaction as a competition for electrons. Since this reaction is spontaneous, $\mathrm{Cu^{2+}}$ is better at gaining electrons than $\mathrm{Zn^{2+}}$ and Zn gives up electrons more readily than copper metal. The differing abilities of these metals to gain or lose electrons create a potential difference (cell potential) that pushes electrons through the external circuit. The more positive the cell potential, the greater the driving force for the redox reaction to occur spontaneously.

The cell potential (also called the electromotive force, EMF) measures the difference in electrical potential energy per unit charge between the two electrodes in a galvanic cell. Its units are volts (V), where 1 V = 1 J/C (joule per coulomb), indicating the amount of energy per unit of charge. A coulomb is a unit of electrical charge where one coulomb (C) is the charge of 6.242 x 10^{18} electrons. Just as water flows spontaneously downhill due to gravity, electrons flow “downhill” from higher to lower potential energy in a galvanic cell, allowing the cell to do electrical work.

A positive cell potential ($E_{\text{cell}} > 0$) indicates that the redox reaction is spontaneous, and electrons will flow through the external circuit from the anode to the cathode. A negative cell potential ($E_{\text{cell}} < 0$) indicates that the reaction is non-spontaneous under those conditions. When $E_{\text{cell}} = 0$, the system is at equilibrium, and no net reaction or electrical work occurs.

Different substances have different tendencies to lose or gain electrons, which affects the voltage measured in a galvanic cell.

For example, if we construct a galvanic cell similar to the $\mathrm{Zn/Cu^{2+}}$ cell but replace copper with cobalt metal and 1 M $\mathrm{Co^{2+}}$ in the cathode compartment, the measured voltage is not 1.10 V but only 0.51 V. This tells us that the difference in potential energy between the valence electrons of cobalt and zinc is smaller by 0.59 V than the difference between copper and zinc.

Standard Cell Potential

The measured cell potential also depends on the concentrations of the reacting species and the temperature of the system. To compare the abilities of different substances to gain or lose electrons, chemists need to measure cell potentials under comparable conditions. To do this, chemists define the standard cell potential (E°_{cell}) as the potential of a cell measured under standard conditions:

- All solutions at 1 M concentration,
- All gases at 1 atm,
- Pure solids or liquids for other substances,
- At a fixed temperature, usually 25°C.

By measuring cell potentials under these conditions, chemists can create a scale of relative potentials to predict both the direction of redox reactions and the magnitude of the driving force for those reactions.

Measuring Standard Cell Potentials

It is not possible to measure the potential of a single electrode in isolation. We can only measure the potential difference between two electrodes in a galvanic cell, similar to how we can only measure enthalpy changes or free energy changes, not their absolute values.

To establish a consistent reference point, chemists use the standard hydrogen electrode (SHE), which has a potential of exactly 0 volts under standard conditions. This allows the measurement of standard reduction potentials for other half-reactions relative to the SHE.

The standard hydrogen electrode (Figure $11.4.1$) consists of:

- A platinum electrode (inert and conductive),
- Immersed in a 1 M solution of $\mathrm{H^+}$,
- With $\mathrm{H_2\,(g)}$ bubbling over the electrode at 1 atm,
- At a temperature of 25 °C.

The half-reaction at the SHE is:

$$\mathrm{2\,H^+\,(aq) + 2\,e^-} \rightarrow \mathrm{H_2\,(g)}$$

The SHE can function as either the anode or cathode, depending on the other half-cell it is paired with in the galvanic cell, allowing measurement of the relative tendency of substances to gain or lose electrons.

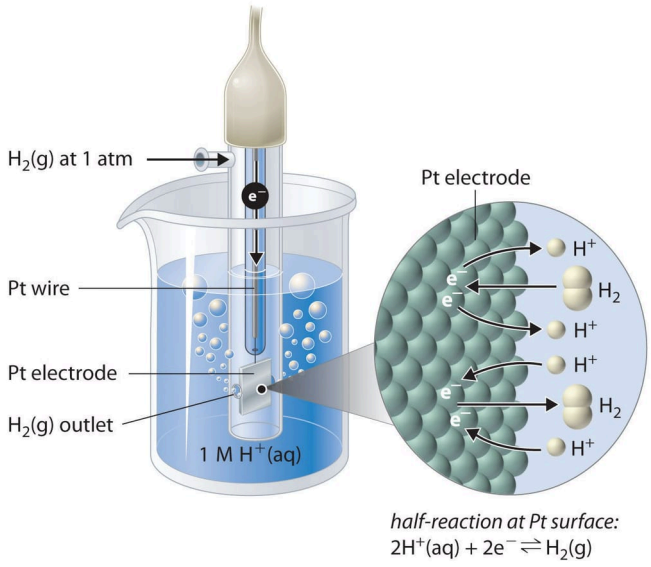


Figure $11.4.1$: The Standard Hydrogen Electrode. The SHE consists of a platinum wire connected to a Pt surface in contact with a 1 M $\mathrm{H^+}$ solution in equilibrium with $\mathrm{H_2\,(g)}$ at 1 atm. The standard potential of the SHE is defined as 0 V under standard conditions.

To measure the standard electrode potential of another half-reaction, we connect the electrode of interest to the SHE in a galvanic cell under standard conditions.

For example, to measure the standard reduction potential of zinc, we can construct the cell (Figure $11.4.2$):

$$\mathrm{Zn\,(s)\ |\ Zn^{2+}\,(aq,\,1\,M)\ ||\ H^+\,(aq,\,1\,M)\ |\ H_2\,(g,\,1\,atm)\ |\ Pt\,(s)}$$

In this setup:

- Zinc is oxidized at the anode: $\mathrm{Zn\,(s)} \rightarrow \mathrm{Zn^{2+}\,(aq) + 2\,e^-}$
- Hydrogen ions are reduced at the cathode: $\mathrm{2\,H^+\,(aq) + 2\,e^-} \rightarrow \mathrm{H_2\,(g)}$

- The voltmeter measures the cell potential of 0.76 V under standard conditions.

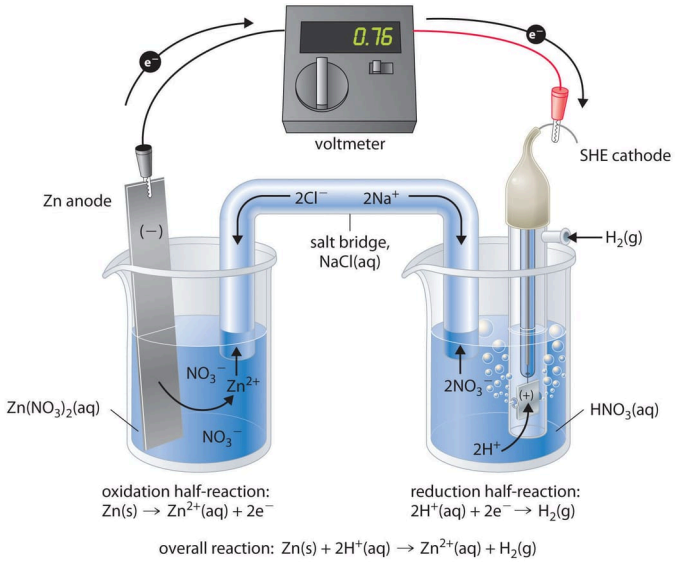


Figure 11.4.2: Measuring a standard electrode potential using the SHE. The voltmeter shows that the standard cell potential of a galvanic cell with a zinc electrode and the SHE is $E^\circ_{\text{cell}} = 0.76\ \text{V}$. Since zinc spontaneously forms $\text{Zn}^{2+}\,(\text{aq})$, while $\text{H}^+\,(\text{aq})$ is reduced to $\text{H}_2\,(\text{g})$, the standard reduction potential for the Zn^{2+}/Zn couple is $-0.76\ \text{V}$.

The standard cell potential can be calculated using:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$$

where:

- E°_{red} is the standard reduction potential for the reduction half-reaction at the cathode
- E°_{ox} is the standard oxidation potential for the oxidation half-reaction at the anode

In the zinc–SHE cell, we measure E°_{cell} = 0.76 V.

We know that the SHE (cathode) reduction potential is E°_{red}= 0.00 V. Zinc is oxidized at the anode, so:

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red}} + E^\circ_{\text{ox}} \\ 0.76\ \text{V} &= 0.00\ \text{V} + E^\circ_{\text{ox}} \\ E^\circ_{\text{ox}} &= 0.76\ \text{V} \end{aligned}$$

Because oxidation is the reverse of reduction, the standard reduction potential for the $\text{Zn}^{2+}\,/\text{Zn}$ couple is the negative of its oxidation potential:

$$E^\circ_{\text{red}} = -E^\circ_{\text{ox}} = -0.76V$$

This process demonstrates how standard reduction potentials are experimentally determined using the SHE as a reference. Chemists have constructed tables of standard reduction potentials for many half-reactions. These values allow us to:

- Predict the direction of redox reactions, and
- Calculate the standard cell potential (E°_{cell}) for many galvanic cells.

Table 11.4.1: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$\text{F}_2\,(\text{g}) + 2\,\text{e}^- \rightarrow 2\,\text{F}^-\,(\text{aq})$	+2.87
$\text{PbO}_2\,(\text{s}) + \text{SO}_4{}^{2-}\,(\text{aq}) + 4\,\text{H}^+\,(\text{aq}) + 2\,\text{e}^- \rightarrow \text{PbSO}_4\,(\text{s}) + 2\,\text{H}_2\text{O}\,(\text{l})$	+1.69
$\text{MnO}_4{}^-\,(\text{aq}) + 8\,\text{H}^+\,(\text{aq}) + 5\,\text{e}^- \rightarrow \text{Mn}^{2+}\,(\text{aq}) + 4\,\text{H}_2\text{O}\,(\text{l})$	+1.51

Half-Reaction	E° (V)
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	+0.56
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.27
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.26
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.35
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.45
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	−0.74
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.19
$Zn(OH)_2(s) + 2e^- \rightarrow Zn(s) + 2OH^-(aq)$	−1.25
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	−2.87
$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$	−2.91
$K^+(aq) + e^- \rightarrow K(s)$	−2.93
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

Interpreting Standard Reduction Potentials

The standard reduction potential of a half-reaction (E°_{red}) measures how readily a species gains electrons under standard

conditions, relative to SHE.

- A more positive E°_{red} means the species is better at gaining electrons. It is more likely to be reduced, and thus acts as a stronger oxidizing agent.
- A more negative E°_{red} means the species is less likely to gain electrons, and the reduced form of the species is a stronger reducing agent.

The standard oxidation potential (E°_{ox}) for a half-reaction is the negative of the standard reduction potential for the reverse reaction:

$$E^\circ_{\text{ox}} = -E^\circ_{\text{red}}$$

A species with a higher E°_{ox} is a stronger reducing agent, because it more readily loses electrons.

For example, the standard reduction potential for the Cu^{2+}/Cu couple is +0.34 V, while for Zn^{2+} / Zn it is −0.76 V. Since +0.34 V > −0.76 V, Cu^{2+} is a stronger oxidizing agent than Zn^{2+}.

Understanding these values allows us to determine:

- Which half-reaction will occur at the cathode (the one with the more positive E°_{red})
- Which will occur at the anode (the one with the less positive E°_{red}, written as an oxidation)

The values of standard reduction potentials also allow us to compare the relative strengths of oxidizing and reducing agents. The figure below summarizes these trends and helps visualize how standard reduction potentials guide predictions about electron flow and spontaneity in galvanic cells.

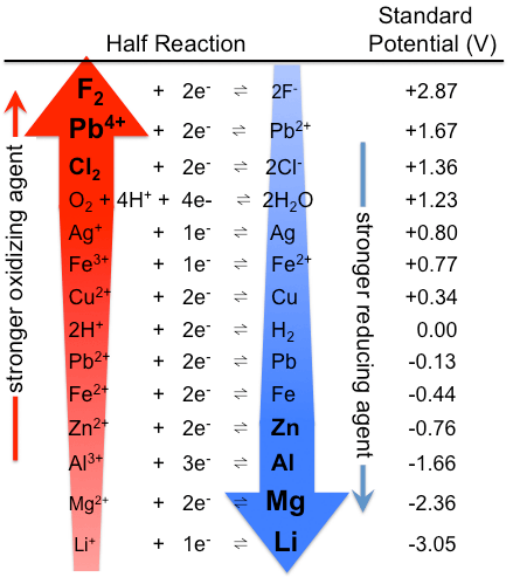


Figure 11.4.3: Species with higher (more positive) standard reduction potentials are stronger oxidizing agents because they more readily gain electrons. The reduced form (products) of species with lower (more negative) standard reduction potentials are stronger reducing agents because they more readily lose electrons. This trend helps predict the direction of electron flow and spontaneity in galvanic cells.(CC BY-SA 3.0; Tem5psu).

Example 11.4.1

Compare Fe^{2+} and Ag^{+} as oxidizing agents, and Fe and Ag as reducing agents, using their standard reduction potentials.

Write the overall spontaneous reaction for a galvanic cell combining the Fe^{2+}/Fe and Ag^{+}/Ag half-cells under standard conditions, and calculate the standard cell potential, E°_{cell}.

Solution

From the standard reduction potential table:

$\mathrm{Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)} \quad E^\circ_{\mathrm{red}} = -0.45\ V$

$\mathrm{Ag^{+}(aq) + e^- \rightarrow Ag(s)} \quad E^\circ_{\mathrm{red}} = +0.80\ V$

- Since $\mathrm{Ag^+}$ has a higher E°_{red} than $\mathrm{Fe^{2+}}$, it is a stronger oxidizing agent.

When we reverse a half-reaction to write it as an oxidation, we change the sign of its E°_{red} to get E°_{ox}. Looking at the oxidation half-reactions:

$\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-} \quad E^\circ_{\mathrm{ox}} = 0.45\ V$

$\mathrm{Ag(s) \rightarrow Ag^{+}(aq) + e^-} \quad E^\circ_{\mathrm{ox}} = -0.80\ V$

- Since Fe has a higher E°_{ox} than Ag, it is a stronger reducing agent.

At the cathode (reduction): $\mathrm{Ag^{+}(aq) + e^- \rightarrow Ag(s)}$

At the anode (oxidation): $\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-}$

To balance electrons, multiply the silver half-reaction by 2:

$2 \times [\mathrm{Ag^{+}(aq) + e^- \rightarrow Ag(s)}]$

Overall cell reaction:

$\mathrm{Fe(s) + 2\,Ag^{+}(aq) \rightarrow Fe^{2+}(aq) + 2\,Ag(s)}$

Calculating E°_{cell}:

$$E^\circ_{cell} = E^\circ_{\mathrm{red}}(\mathrm{cathode}) + E^\circ_{\mathrm{ox}}(\mathrm{anode}) = 0.80\,V + 0.45\,V = 1.25\,V$$

Because $E^\circ_{\mathrm{cell}} > 0$, the reaction is spontaneous under standard conditions.

Exercise 11.4.1

Compare $\mathrm{Cu^{2+}}$ and $\mathrm{Zn^{2+}}$ as oxidizing agents, and Cu and Zn as reducing agents, using standard reduction potentials. Write the overall reaction for a galvanic cell made with $\mathrm{Cu^{2+}/Cu}$ and $\mathrm{Zn^{2+}/Zn}$ half-cells under standard conditions and calculate the standard cell potential, E°_{cell}.

Given:

$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)} \quad E^\circ_{\mathrm{red}} = +0.34\ V$

$\mathrm{Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)} \quad E^\circ_{\mathrm{red}} = -0.76\ V$

Answer available at the end of this section.

Calculating Standard Cell Potentials

Once the anode and cathode are identified, the standard cell potential can be calculated:

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{red}} + E^\circ_{\mathrm{ox}}$$

or equivalently:

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{red,\ cathode}} - E^\circ_{\mathrm{red,\ anode}}$$

Both forms are valid; the first makes it explicit that one half-reaction is written as an oxidation, the other as a reduction.

Cell potential (voltage) is the potential energy per unit charge, so it is an intensive property. This means it does not depend on the amount of substance or the number of electrons transferred. As a result, E° values are independent of the stoichiometric coefficients used in the half-reaction. The coefficients needed to balance the overall redox reaction do not affect the value of the cell potential, even though they determine the total charge and energy transferred during the reaction.

A positive standard cell potential ($E^\circ_{\text{cell}} > 0$) indicates that the redox reaction is spontaneous under standard conditions, and electrons will flow through the external circuit from the anode to the cathode. A negative cell potential ($E^\circ_{\text{cell}} < 0$) indicates that the redox reaction is non-spontaneous under those conditions.

Example 11.4.2: Cell Potentials from Standard Reduction Potentials

Consider a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells.

What is the standard cell potential for the galvanic cell?

What is the overall redox reaction that occurs in the cell?

Identify the oxidizing and reducing agents.

Solution

a) Using Table 11.4.1, the reactions involved in the galvanic cell, both written as reductions, are

$$\text{Au}^{3+}(\text{aq}) + 3\,\text{e}^- \rightarrow \text{Au}(\text{s}) \quad E^\circ_{\text{red}} = +1.50\ \text{V}$$

$$\text{Ni}^{2+}(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Ni}(\text{s}) \quad E^\circ_{\text{red}} = -0.26\ \text{V}$$

Galvanic cells have positive cell potentials for spontaneous reactions. The half-reaction with the more positive standard reduction potential occurs at the cathode, while the one with the more negative potential occurs at the anode (as an oxidation).

Reverse the anode half-reaction and switch the sign of E°_{red} to find E°_{ox}:

$$\begin{aligned} &\text{Anode (oxidation): } \text{Ni}(\text{s}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\,\text{e}^- \quad E^\circ_{\text{ox}} = -E^\circ_{\text{red}} = +0.26\ \text{V} \\ &\text{Cathode (reduction): } \text{Au}^{3+}(\text{aq}) + 3\,\text{e}^- \rightarrow \text{Au}(\text{s}) \quad E^\circ_{\text{red}} = +1.50\ \text{V} \end{aligned}$$

To balance the electrons, multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2:

$$\begin{array}{ll} \text{Anode (oxidation): } 3\text{Ni}(\text{s}) \rightarrow 3\text{Ni}^{2+}(\text{aq}) + 6\,\text{e}^- & E^\circ_{\text{ox}} = -E^\circ_{\text{red}} = +0.26\ \text{V} \\ \text{Cathode (reduction): } 2\text{Au}^{3+}(\text{aq}) + 6\,\text{e}^- \rightarrow 3\text{Au}(\text{s}) & E^\circ_{red} = +1.50\ \text{V} \\ \hline \text{Overall reaction: } 3\,\text{Ni}(\text{s}) + 2\,\text{Au}^{3+}(\text{aq}) \rightarrow 3\,\text{Ni}^{2+}(\text{aq}) + 2\,\text{Au}(\text{s}) & E^\circ_{cell} = +1.76\ \text{V} \end{array}$$

The reduction potentials are **not scaled** by the stoichiometric coefficients when calculating the standard cell potential:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = 1.50\ \text{V} + 0.26\ \text{V} = 1.76\ \text{V}$$

From the half-reactions, nickel (Ni) is oxidized, so it is the reducing agent. Gold (III) ions (Au^{3+}) are reduced, so they are the oxidizing agent.

Exercise 11.4.2

A galvanic cell consists of an Mg electrode in 1 M $\text{Mg}(\text{NO}_3)_2$ solution and an Ag electrode in 1 M AgNO_3 solution. Calculate the standard cell potential at 25 °C.

Answer available at the end of this section.

Example 11.4.3

A galvanic cell with a measured standard cell potential of 0.27 V at 25 °C is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal in 1 M $\mathrm{GaCl_3}$, and the other contains a piece of nickel in 1 M $\mathrm{NiCl_2}$. When connected:

- Gallium oxidizes at the anode:

$$\mathrm{Ga\,(s)} \rightarrow \mathrm{Ga^{3+}\,(aq)} + 3\,\mathrm{e^-}$$

- Nickel ions are reduced at the cathode:

$$\mathrm{Ni^{2+}\,(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Ni\,(s)}$$

If the oxidation potential for gallium under standard conditions is +0.55 V, calculate the standard reduction potential for $\mathrm{Ni^{2+}/Ni}$ under standard conditions.

Solution:

Given:

- $E^\circ_{\text{cell}} = 0.27\ \text{V}$
- $E^\circ_{\text{ox}} = +0.55\ \text{V}$

We use the relationship:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$$

Solving for the unknown reduction potential:

$$E^\circ_{\text{red}} = E^\circ_{\text{cell}} - E^\circ_{\text{ox}} = 0.27\,\text{V} - 0.55\,\text{V} = -0.28\,\text{V}$$

Thus, the standard reduction potential for $\mathrm{Ni^{2+}/Ni}$ is:

$$E^\circ_{\text{red}} = -0.28\,\text{V}$$

Exercise 11.4.3

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $\mathrm{Hg(CH_3CO_2)_2}$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $\mathrm{MgCl_2}$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode:

$$\mathrm{Hg^{2+}\,(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Hg\,(l)}$$

- anode:

$$\mathrm{Mg\,(s)} \rightarrow \mathrm{Mg^{2+}\,(aq)} + 2\,\mathrm{e^-}$$

If the potential for the oxidation of Mg to $\mathrm{Mg^{2+}}$ under standard conditions is 2.37 V, what is the standard reduction potential for the reaction that occurs at the cathode?

Answer available at the end of this section.

Summary

The cell potential (E_{cell}) is a measure of the driving force for the reaction. The voltage (cell potential) in a galvanic cell depends on the identity of the reacting substances, their concentrations, and the temperature. The cell potential under standard conditions (1

M for solutions, 1 atm for gases, pure solids or liquids for other substances) is called the standard cell potential (E°_{cell}).

Because we can only measure potential differences between electrodes, chemists use the Standard Hydrogen Electrode (SHE) as a reference, assigning it a potential of 0 V. This allows the determination of standard reduction potentials (E°_{red}) for many half-reactions.

The standard oxidation potential of a half-reaction is equal in magnitude and opposite in sign to its reduction potential. Importantly, because voltage is an intensive property, standard cell potentials do not depend on the stoichiometric coefficients used to balance the overall redox reaction.

The standard cell potential for a galvanic cell can be calculated using:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$$

A positive standard cell potential ($E^\circ_{\text{cell}} > 0$) indicates that the redox reaction is spontaneous under standard conditions, with electrons flowing through the external circuit from the anode to the cathode.

Standard reduction potentials can also be used to compare the relative strengths of oxidizing and reducing agents and to predict which redox reactions will be spontaneous under standard conditions.

Glossary

cell potential (E_{cell})
: The difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions; also called electromotive force (EMF).

standard cell potential ($E°_{\text{cell}}$)
: The cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 M for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode.

standard hydrogen electrode (SHE)
: An electrode that consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials..

standard oxidation potential ($E°_{\text{ox}}$)
: Measures how readily a substance loses electrons under standard conditions; the negative of the standard reduction potential for the reverse reaction.

standard reduction potential ($E°_{\text{red}}$)
: Measures how readily a species gains electrons under standard conditions (1 bar or 1 atm for gases; 1 M for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials.

Answers

Exercise 11.4.1

Cu^{2+} has a higher E°_{red} than Zn^{2+}, so it is the stronger oxidizing agent.

Zn has a higher E°_{ox} (looking at the reverse reaction) than Cu, so it is the stronger reducing agent.

At the cathode (reduction):

$\text{Cu}^{2+}(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Cu}(\text{s}) \quad E^\circ_{\text{red}} = +0.34\ V$

At the anode (oxidation):

$\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\,\text{e}^- \quad E^\circ_{\text{ox}} = +0.76\ V$

Overall cell reaction:

$\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

Calculating the standard cell potential:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) + E^\circ_{\text{ox}}(\text{anode}) = 0.34\,V + 0.76\,V = 1.10\,V$$

Since $E^\circ_{\text{cell}} > 0$, the reaction is spontaneous under standard conditions.

Exercise 11.4.2

$$\mathrm{Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)} \quad E^\circ_{red} = -2.37\ \mathrm{V}$$
$$\mathrm{Ag^{+}(aq) + e^- \rightarrow Ag(s)} \quad E^\circ_{red} = +0.80\ \mathrm{V}$$

Since the cell is galvanic, the element with the more negative reduction potential will undergo oxidation at the anode. We reverse the anode half-reaction and switch the sign of E°_{red} to find E°_{ox}:

$$\begin{array}{ll} \text{Anode (oxidation): } \mathrm{Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^-} & E^\circ_{ox} = -E^\circ_{red} = +2.37\ \mathrm{V} \\ \text{Cathode (reduction): } \mathrm{2Ag^{+}(aq) + 2\,e^- \rightarrow 2Ag(s)} & E^\circ_{red} = +0.80\ \mathrm{V} \\ \hline \text{Overall reaction: } \mathrm{Mg(s) + 2\,Ag^{+}(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)} & E^\circ_{cell} = +3.17\ \mathrm{V} \end{array}$$

The standard cell potential is:

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = 0.80\ \mathrm{V} + 2.37\ \mathrm{V} = 3.17\ \mathrm{V}$$

Exercise 11.4.3

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{red} + E^\circ_{ox} \\ 3.22\ \mathrm{V} &= E^\circ_{red} + 2.37\ \mathrm{V} \\ E^\circ_{red} &= 0.85\ \mathrm{V} \end{aligned}$$

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11.5: Connecting Cell Potential, Free Energy, and Equilibrium

Learning Objectives

- Relate cell potentials to free energy changes.
- Relate standard cell potentials to equilibrium constants.
- Interconvert standard cell potential, standard free energy change and equilibrium constant, and assess the spontaneity of a redox reaction under standard state conditions.

In this section, we will explore the connections between cell potential, free energy, and the equilibrium constant for redox reactions. In the previous section, we saw that cell potential can predict the spontaneity of a redox reaction. From the thermodynamics chapter, we know that spontaneity is also predicted by free energy changes, and that the standard free energy change is related to the equilibrium constant. Since electrons flowing through a galvanic cell can do work, the electrical work produced relates directly to the cell's potential and the free energy change of the redox process. This section brings these ideas together, showing how cell potential, free energy, and equilibrium are connected in galvanic cells.

The Relationship between Cell Potential & Gibbs Energy

The electric work done by a galvanic cell is equal to the product of the total electrical charge transferred and the cell potential:

$$w_{\text{electric}} = -nFE_{\text{cell}}$$

where:

- n = stoichiometric coefficient of electrons transferred in the balanced redox reaction.
- F = Faraday constant, $96485\ \text{C/mol e}^-$.
- nF = total charge transferred per one mole of the redox reaction as written, in coulombs per mol (C/mol).
- The negative sign indicates that the cell does work on the surroundings.

The maximum non-expansion work a chemical system can do equals the change in free energy:

$$\Delta G = w_{\text{max}}$$

Therefore, the relationship between cell potential and Gibbs free energy is:

$$\Delta G = -nFE_{\text{cell}} \tag{11.5.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG and a positive value of E_{cell}, consistent with our earlier discussions.

Under standard state conditions:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \tag{11.5.2}$$

A spontaneous redox reaction will have $\Delta G^\circ < 0$ and $E^\circ_{\text{cell}} > 0$ under standard state conditions.

Michael Faraday (1791–1867)

Michael Faraday was a British physicist and chemist, and one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was largely self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. Many of the specialized terms introduced in this chapter (electrode, anode, cathode, and more) are due to Faraday. In addition,

he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for The Chemical History of a Candle, a series of public lectures on the chemistry and physics of flames. The Faraday constant, used in this section, is named in his honour.

Example 11.5.1

Suppose you want to prepare elemental bromine (Br_2) from bromide (Br^-) using the dichromate ion ($Cr_2O_7^{2-}$) as an oxidizing agent. Using the data below, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

$$\begin{aligned} Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- &\rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) & E^\circ_{red} &= 1.36\ V \\ Br_2(l) + 2\,e^- &\rightarrow 2\,Br^-(aq) & E^\circ_{red} &= 1.09\ V \end{aligned}$$

Given: standard reduction potentials

Asked for: ΔG° for the reaction and spontaneity

Strategy:

A. Use the relevant half-reactions and their E°_{cell} values to write the overall reaction and calculate E°_{cell}.
B. Determine the number of electrons transferred in the overall reaction and use Equation 11.5.2 to calculate ΔG°.

Solution

A. Write the relevant half-reactions. The dichromate ion is the oxidizing agent (reduction half-reaction), and since we want to produce Br_2, the bromine half-reaction must be reversed to an oxidation:

$$\begin{aligned} &\text{reduction:} & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- &\rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^\circ_{red} &= 1.36\ V \\ &\text{oxidation:} & 2Br^-(aq) &\rightarrow Br_2(l) + 2e^- & E^\circ_{ox} &= -1.09\ V \end{aligned}$$

To balance electrons, multiply the oxidation half-reaction by 3. Standard electrode potentials are intensive properties and do not change when the half-reaction is multiplied by a factor for balancing purposes.

$$\begin{aligned} &\text{reduction:} & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- &\rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^\circ_{red} &= 1.36\ V \\ &\text{oxidation:} & 3(2Br^-(aq) &\rightarrow Br_2(l) + 2e^-) & E^\circ_{ox} &= -1.09\ V \\ &\text{overall:} & Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) &\rightarrow 2Cr^{3+}(aq) + 3Br_2(l) + 7H_2O(l) & E^\circ_{cell} &= 0.27\ V \end{aligned}$$

B. Calculate ΔG° using Equation 11.5.2. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned} \Delta G^\circ &= -(n)(F)(E^\circ_{cell}) \\ &= -(6)(96,485\ J/(V \cdot mol))(0.27\ V) \\ &= -1.6 \times 10^5\ J/mol \end{aligned}$$

The reaction is spontaneous under standard state conditions because $\Delta G^\circ < 0$ and $E^\circ > 0$.

Exercise 11.5.1

Calculate ΔG° for the reduction of ferric ion by iodide:

$$2\,Fe^{3+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)$$

Is the reaction spontaneous under standard state conditions?

$$\begin{aligned} Fe^{3+}(aq) + e^- &\rightarrow Fe^{2+}(aq) & E^\circ_{red} &= 0.771\ V \\ I_2(s) + 2\,e^- &\rightarrow 2\,I^-(aq) & E^\circ_{red} &= 0.536\ V \end{aligned}$$

Answer available at the end of this section.

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between the standard free energy change (ΔG°) and the equilibrium constant (K), to find a direct connection between the standard cell potential (E°_{cell}) and K. Recall from the thermodynamics chapter that:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 11.5.2), we can write

$$-nFE^\circ_{\text{cell}} = -RT \ln K$$

Rearranging to solve E°_{cell}:

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{11.5.3}$$

At $T = 298\ K$, this simplifies to:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\ &= \left[\frac{[8.314\ \text{J/(mol} \cdot \text{K)(298 K)}]}{n[96,485\ \text{J/(V} \cdot \text{mol)}]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \end{aligned}$$

where log is the base-10 logarithm. Note: 0.0592 V comes from substituting values for R, T, and, F at 298 K, and converting ln to $\log_{10}$.

Thus, the standard cell potential is directly proportional to the logarithm of the equilibrium constant:

- A large K value (favouring products) corresponds to a large, positive E°_{cell}
- A small K value (favouring reactants) correspond to a small or negative E°_{cell}

Example 11.5.2

When a car battery loses its charge (for example, if a car is left unused), metallic lead (Pb) reacts with PbO_2 in the presence of sulfate ions ($\text{SO}_4{}^{2-}$) to give PbSO_4. What is the equilibrium constant for this reaction?

$$\begin{aligned} \text{PbO}_2\,(\text{s}) + \text{SO}_4{}^{2-}\,(\text{aq}) + 4\,\text{H}^+\,(\text{aq}) + 2\,\text{e}^- &\rightleftharpoons \text{PbSO}_4\,(\text{s}) + 2\,\text{H}_2\text{O}\,(\text{l}) \qquad E^\circ_{\text{red}} = 1.69\ \text{V} \\ \text{PbSO}_4\,(\text{s}) + 2\,\text{e}^- &\rightleftharpoons \text{Pb}\,(\text{s}) + \text{SO}_4{}^{2-}\,(\text{aq}) \qquad E^\circ_{\text{red}} = -0.36\ \text{V} \end{aligned}$$

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^o_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 11.5.3 to solve for K.

Solution

A. Use the reduction half-reactions to find the overall reaction. Since Pb is a reactant, the second half-reaction must be reversed to an oxidation:

$$\begin{aligned} &\text{reduction: } \text{PbO}_2\,(\text{s}) + \text{SO}_4{}^{2-}\,(\text{aq}) + 4\,\text{H}^+\,(\text{aq}) + 2\,\text{e}^- \rightleftharpoons \text{PbSO}_4\,(\text{s}) + 2\,\text{H}_2\text{O}\,(\text{l}) \qquad E^\circ_{\text{red}} = 1.69\ \text{V} \\ &\text{oxidation: } \text{Pb}\,(\text{s}) + \text{SO}_4{}^{2-}\,(\text{aq}) \rightleftharpoons \text{PbSO}_4\,(\text{s}) + 2\,\text{e}^- \qquad E^\circ_{\text{ox}} = 0.36\ \text{V} \\ &\text{overall: } \text{Pb}\,(\text{s}) + 2\,\text{SO}_4{}^{2-}\,(\text{aq}) + \text{PbO}_2\,(\text{s}) + 4\,\text{H}^+\,(\text{aq}) \rightleftharpoons 2\,\text{PbSO}_4\,(\text{s}) + 2\,\text{H}_2\text{O}\,(\text{l}) \qquad E^\circ_{\text{cell}} = 2.05\ \text{V} \end{aligned}$$

B. Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 11.5.3 for K:

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K$$
$$\frac{nFE^\circ_{\text{cell}}}{RT} = lnK$$
$$K = e^{\frac{nFE^\circ_{\text{cell}}}{RT}}$$

$$K = e^{\frac{(2)(96500\ \text{C/mol})(2.05\ \text{J/C})}{8.314\ (\text{J/(molK)})(298\ \text{K})}} = 2.26 \times 10^{69}$$

The equilibrium lies far to the right, favouring the formation of products. This large equilibrium constant indicates that the redox reaction proceeds nearly to completion, leaving few reactants. This means that if a car battery is left unused for a long time, the reaction goes nearly to completion, leaving the battery unable to start the car.

Exercise 11.5.2

Calculate the equilibrium constant for the reaction of $\text{Sn}^{2+}\,(\text{aq})$ with oxygen to produce $\text{Sn}^{4+}\,(\text{aq})$ and water:

$$2\,\text{Sn}^{2+}\,(\text{aq}) + \text{O}_2\,(\text{g}) + 4\,\text{H}^+\,(\text{aq}) \rightleftharpoons 2\,\text{Sn}^{4+}\,(\text{aq}) + 2\,\text{H}_2\text{O}\,(\text{l})$$

$$\text{Sn}^{4+}\,(\text{aq}) + 2\,\text{e}^- \rightleftharpoons \text{Sn}^{2+}\,(\text{aq}) \qquad E^\circ_{\text{red}} = 0.15\ \text{V}$$
$$\text{O}_2\,(\text{g}) + 4\,\text{H}^+\,(\text{aq}) + 4\,\text{e}^- \rightleftharpoons 2\,\text{H}_2\text{O}\,(\text{l}) \qquad E^\circ_{\text{red}} = 1.23\ \text{V}$$

Answer available at the end of this section.

Figure 11.5.1 summarizes how the standard cell potential (E°_{cell}), standard free energy change (ΔG°), and equilibrium constant (K) are mathematically connected. Table 11.5.1 correlates the direction of spontaneity with these quantities.

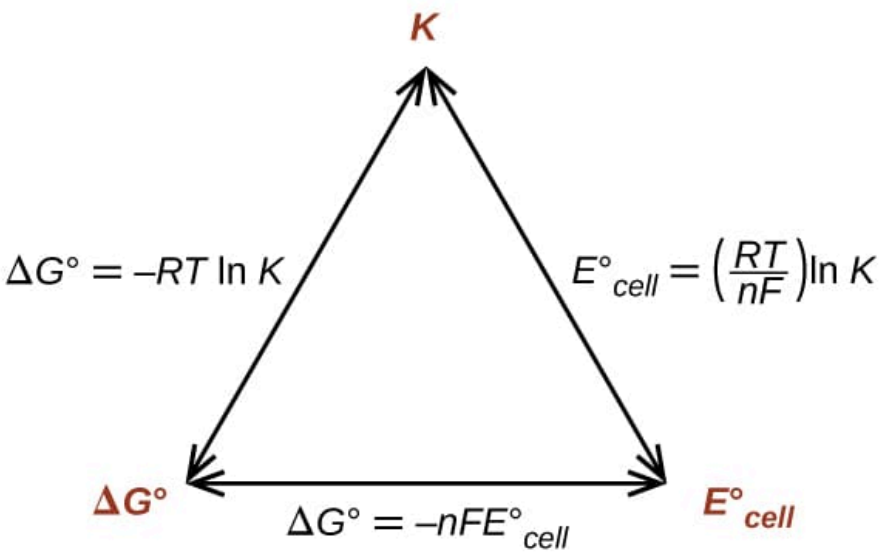


Figure 11.5.1: A triangular diagram showing how the equilibrium constant (K), standard free energy change (ΔG°), and standard cell potential (E°_{cell}) are mathematically related under standard conditions.

Table 11.5.1: Relationship between K, ΔG°, and E°_{cell} under standard conditions.

K	ΔG°	E°_{cell}	Comment
> 1	< 0	> 0	Reaction is spontaneous under standard conditions; products are more abundant at equilibrium.
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions; reactants are more abundant at equilibrium.
$= 1$	$= 0$	$= 0$	System is at equilibrium under standard state conditions; reactants and products are equally abundant.

Summary

A positive cell potential (E_{cell}) indicates that a redox reaction is spontaneous under standard conditions, while a negative value indicates non-spontaneity.

The maximum electrical work a galvanic cell can do equals the free energy change (ΔG) of the reaction:

$$\Delta G = -nFE_{\text{cell}}$$

where n is the number of electrons transferred in the balanced reaction and F is Faraday's constant ($96,485\ \text{C/mol e}^-$).
Under standard conditions:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

A negative ΔG° corresponds to a positive E°_{cell}, indicating the redox reaction is spontaneous under standard state conditions.

The relationship between the standard cell potential and the equilibrium constant (K) is:

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right)\ln K$$

A large value of K (favouring products) corresponds to a large, positive E°_{cell}, while a small value of K (favouring reactants) corresponds to small or negative E°_{cell}.

Glossary

electric work (w_{electric})

The negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG).

Faraday's constant (F)

The charge on 1 mol of electrons; F = 96,485 C/mol e^-.

Answers

Exercise 11.5.1

$$\begin{aligned} 2\,\text{Fe}^{3+}(\text{aq}) + 2\,\text{e}^- &\rightarrow 2\,\text{Fe}^{2+}(\text{aq}) & E^\circ_{\text{red}} &= 0.771\ \text{V} \\ 2\,\text{I}^-(\text{aq}) &\rightarrow \text{I}_2(\text{s}) + 2\,\text{e}^- & E^\circ_{\text{ox}} &= -0.536\ \text{V} \\ 2\,\text{Fe}^{3+}(\text{aq}) + 2\,\text{I}^-(\text{aq}) &\rightarrow 2\,\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s}) & E^\circ_{\text{cell}} &= 0.235\ \text{V} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= -(n)(F)(E^\circ_{\text{cell}}) \\ &= -(2)(96,485\ \text{J/(V}\cdot\text{mol)})(0.235\ \text{V}) \\ &= -4.53\times10^4\ \text{J/mol} \end{aligned}$$

The reaction is spontaneous under standard state conditions.

Exercise 11.5.2

$$\begin{aligned} 2\,\text{Sn}^{2+}(\text{aq}) &\rightleftharpoons 2\,\text{Sn}^{4+}(\text{aq}) + 4\,\text{e}^- & E^\circ_{\text{ox}} &= -0.15\ \text{V} \\ \text{O}_2(\text{g}) + 4\,\text{H}^+(\text{aq}) + 4\,\text{e}^- &\rightleftharpoons 2\,\text{H}_2\text{O}(\text{l}) & E^\circ_{\text{red}} &= 1.23\ \text{V} \\ 2\,\text{Sn}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\,\text{H}^+(\text{aq}) &\rightleftharpoons 2\,\text{Sn}^{4+}\ 2\,\text{H}_2\text{O}(\text{l}) & E^\circ_{\text{cell}} &= 1.08\ \text{V} \end{aligned}$$

$$K = e^{\frac{nFE^\circ_{\text{cell}}}{RT}}$$

$$K = e^{\frac{(4)(96500\ \text{C/mol})(1.08\ \text{J/C})}{8.314\ \text{(J/(molK)}(298\ \text{K})}} = 1.18\times10^{73}$$

This large equilibrium constant indicates that the redox reaction proceeds nearly to completion, leaving few reactants.

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11.6: Cell Potentials Beyond Standard Conditions

Learning Objectives

- Calculate cell potentials under non-standard conditions using the Nernst equation.
- Explain how concentration differences generate voltage in concentration cells.
- Use cell potentials to determine unknown concentrations in solution.

In real-world applications, redox reactions and galvanic cells rarely operate under standard conditions. The concentrations of reactants and products often vary, which affects the cell potential and the direction of the reaction. For example, the voltage of a galvanic cell decreases as the redox reaction proceeds because reactants are consumed and products are formed.

The Nernst Equation allows us to calculate the actual cell potential under non-standard conditions by relating the cell potential to the concentrations of reactants and products through the reaction quotient. This equation is one of the most important tools in electrochemistry, allowing us to:

- Predict the direction of a redox reaction under any conditions.
- Calculate the voltage of a galvanic cell as it operates.
- Determine equilibrium constants from electrochemical data.

By understanding and applying the Nernst Equation, we can bridge the connections between concentration, equilibrium, free energy, and cell potential, providing a complete picture of how electrochemical cells behave in real-world scenarios.

The Nernst Equation: Calculating Cell Potential Under Non-Standard Conditions

We have seen that under standard conditions, the free energy change and the cell potential are related by:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

and that the standard free energy change (ΔG°) is linked to the equilibrium constant by:

$$\Delta G^\circ = -RT \ln K$$

Under non-standard conditions, the free energy change (ΔG) is:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient for the reaction at current concentrations (not equilibrium).

Since:

$$\Delta G = -nFE_{\text{cell}}$$

and

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

we can combine these to give:

$$-nFE_{cell} = -nFE^\circ_{\text{cell}} + RT \ln Q$$

Dividing both sides by $-nF$ gives the Nernst Equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{11.6.1}$$

At $T = 298\ \text{K}$ (room temperature), using $R = 8.314\ \text{J/(mol} \cdot \text{K)}$ and $F = 96,485\ \text{C/mol}$, and converting to base-10 logarithms, the Nernst Equation simplifies to:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\,V}{n} \log Q \tag{11.6.2}$$

- n: number of electrons transferred in the balanced redox reaction
- Q: reaction quotient using current concentrations
- E_{cell}: cell potential under current (non-standard) conditions
- E°_{cell}: standard cell potential

This relationship, derived by the German physicist and chemist Walter Nernst (1864–1941), allows us to calculate how the cell potential changes as concentrations change, predict the direction of redox reactions under any conditions, and determine equilibrium constants from electrochemical data.

At equilibrium, there is no net transfer of electrons, and the cell potential is zero ($E_{\text{cell}} = 0$). The Nernst Equation then reduces to:

$$0 = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln K$$

or rearranged,

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

showing the direct link between the standard cell potential and the equilibrium constant of a redox reaction.

Example 11.6.1

The following redox reaction proceeds spontaneously under standard conditions because $E^\circ_{\text{cell}} > 0$, which means $\Delta G^\circ < 0$:

$$2\,\text{Ce}^{4+}\,(\text{aq}) + 2\,\text{Cl}^-\,(\text{aq}) \longrightarrow 2\,\text{Ce}^{3+}\,(\text{aq}) + \text{Cl}_2\,(\text{g}) \quad E^\circ_{\text{cell}} = 0.25\,V$$

Calculate E_{cell} under the following conditions and determine whether the reaction is spontaneous:

- $[\text{Ce}^{4+}] = 0.013\ \text{M}$
- $[\text{Ce}^{3+}] = 0.60\ \text{M}$
- $[\text{Cl}^-] = 0.0030\ \text{M}$
- $P_{\text{Cl}_2} = 1.0\ \text{atm}$
- $T = 25^\circ\text{C}$

Strategy

Determine the number of electrons transferred (n), then use the Nernst equation at 298 K to calculate the cell potential under these conditions:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

Solution

From the half-reactions:

$$\text{Ce}^{4+}\,(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}\,(\text{aq})$$

$$2\,\text{Cl}^-\,(\text{aq}) \rightarrow \text{Cl}_2\,(\text{g}) + 2\,\text{e}^-$$

we see that $n = 2$ electrons are transferred.

Next, write the reaction quotient (Q):

$$Q = \frac{[Ce^{3+}]^2\ P_{Cl_2}}{[Ce^{4+}]^2\ [Cl^-]^2}$$

Substitute the given values:

$$Q = \frac{(0.60)^2(1.0)}{(0.013)^2(0.0030)^2} = 2.37 \times 10^8$$

Now, apply the Nernst equation:

$$E_{\text{cell}} = 0.25\,V - \frac{(8.314\,J/(mol \cdot K))(298\,K)}{(2)(96485\,C/mol)}\ln(2.37 \times 10^8) = 0.00\,V$$

The cell potential under these conditions is $0.00\ V$, indicating that the system is at equilibrium. The reaction proceeds spontaneously in both directions under these conditions, and no net electrical work is done.

Exercise 11.6.1

Molecular oxygen will not oxidize MnO_2 to permanganate (MnO_4^-) via the following reaction under standard state conditions:

$$4\,MnO_2\,(s) + 3\,O_2\,(g) + 4\,OH^-\,(aq) \rightleftharpoons 4\,MnO_4^-\,(aq) + 2\,H_2O\,(l) \quad E^\circ_{\text{cell}} = -0.20\ V$$

Calculate E_{cell} for the reaction under the following conditions and determine whether the reaction will occur spontaneously:

- pH = 10.00
- P_{O_2}= 0.20 atm
- [MnO_4^-] = 1.0 × 10^{-4} M
- $T = 25^\circ C$.

Answer available at the end of this section.

Cell Potential and Reaction Progress

As a galvanic cell operates and the reaction proceeds, reactants are converted to products. This causes the electrochemical drive of the reaction to decrease, observed as a decrease in the cell potential.

For example, consider this galvanic cell:

$$Zn\,(s)\,|\,Zn^{2+}\,(aq)\,\|\,Cu^{2+}\,(aq)\,|\,Cu\,(s)$$

with the overall reaction:

$$Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s) \quad E^\circ_{cell} = 1.10V$$

The reaction quotient is:

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0 × 10^{-6} M Zn^{2+}. At 298 K, the cell potential can be calculated from Equation 11.6.2:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$
$$= 1.10\ \text{V} - \left(\frac{0.0592\ \text{V}}{2}\right)\log\left(\frac{1.0\times10^{-6}}{1.0}\right) = 1.28\ \text{V}$$

This initial voltage is greater than E°_{cell} because $Q < 1$, making the $\ln Q$ term negative.

As the reaction proceeds, $[\text{Zn}^{2+}]$ increases as the zinc electrode oxidizes, while $[\text{Cu}^{2+}]$ decreases as copper deposits on the electrode. This increases Q and the cell voltage decreases. When $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$, $Q = 1$ and $E_{\text{cell}} = E^\circ_{\text{cell}}$ = 1.10 V.

If the reaction continues further, $[\text{Zn}^{2+}]$ continues to increase while $[Cu^{2+}]$ decreases, causing Q to increase further and the voltage to continue dropping. If neither electrode is fully consumed (breaking the circuit), the cell voltage will eventually reach zero, indicating the reaction has reached equilibrium and the battery is considered "dead". At equilibrium:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0592\ \text{V}}{n}\right)\log Q = 0$$
$$E^\circ = \left(\frac{0.0592\ \text{V}}{n}\right)\log K$$
$$\log K = \frac{nE^\circ}{0.0592\ \text{V}} = \frac{2(1.10\ \text{V})}{0.0592\ \text{V}} = 37.23$$
$$K = 10^{37.23} = 1.7\times10^{37}$$

This very large K indicates that the reaction strongly favours products at equilibrium.

Figure 11.6.1 shows how the cell potential for the Zn/Cu^{2+} cell changes as a function of the reactant quotient (on a logarithmic scale). The slope of the plot is –0.0591/n.

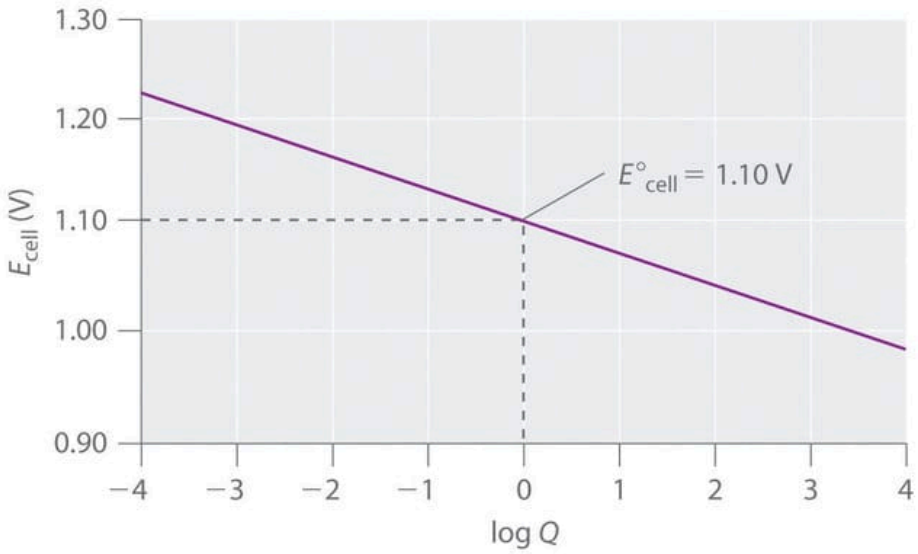


Figure 11.6.1: Variation of E_{cell} with log Q for a Zn/Cu^{2+} cell . Initially, $\log Q < 0$, so $E_{\text{cell}} > E^\circ_{\text{cell}}$. As the reaction progresses, $\log Q$ increases, and E_{cell} decreases. When $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$, $\log Q$ = 0 and $E_{\text{cell}} = E^\circ_{\text{cell}} = 1.10V$. As the reaction continues, $\log Q$ continues to increase until $Q = K$ and the cell voltage reaches zero, indicating that the system has reached equilibrium.

Chemistry in Everyday Life: Fuel Cells

Fuel cells are galvanic cells that continuously convert chemical energy into electrical energy as long as fuel is supplied. Unlike batteries, which store a fixed amount of reactants internally, fuel cells require a constant input of fuel (often hydrogen) and an oxidant (often oxygen).

Fuel cells use the same redox chemistry as combustion but in a controlled, electrochemical process, making them significantly more efficient and cleaner. For example, hydrogen fuel cells produce only water as a byproduct while delivering electricity to power devices, vehicles, and even space missions.

In a typical hydrogen fuel cell, hydrogen gas enters the anode side, where it is oxidized:
anode: $2\,\mathrm{H_2\,(g)} \rightarrow 4\,\mathrm{H^+\,(aq)} + 4\,\mathrm{e^-}$

At the cathode, oxygen gas from the air is reduced:
cathode: $\mathrm{O_2\,(g)} + 4\,\mathrm{H^+\,(aq)} + 4\,\mathrm{e^-} \rightarrow 2\,\mathrm{H_2O\,(l)}$

The overall cell reaction is:
cell: $2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \rightarrow 2\,\mathrm{H_2O\,(l)} \quad E_{\text{cell}} \approx +1.2\ \mathrm{V}$

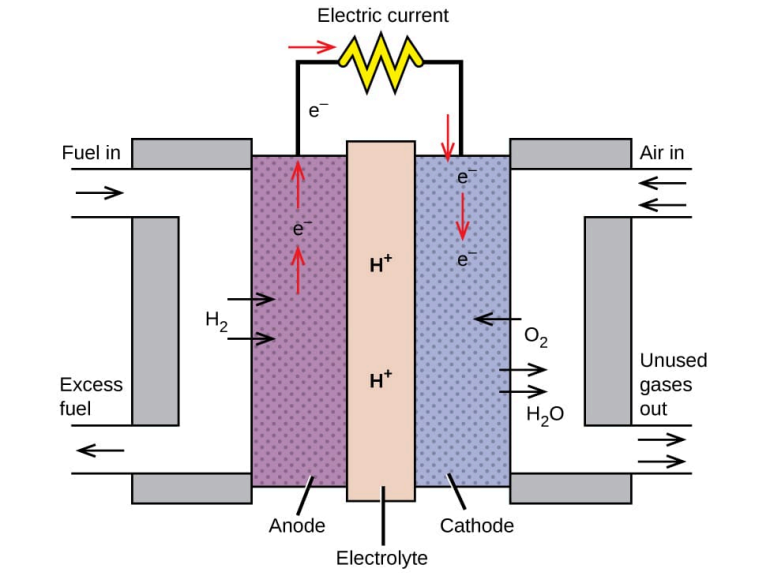


Figure 11.6.2: In a hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.

The voltage of a hydrogen fuel cell is typically around 1.2 V under standard conditions, but the actual cell potential depends on the partial pressures of $\mathrm{H_2}$ and $\mathrm{O_2}$, which can be analyzed using the Nernst equation. By increasing the pressure of hydrogen and oxygen, the fuel cell can operate at a higher potential, improving its efficiency while remaining environmentally friendly.

Fuel cells are often twice as efficient as internal combustion engines, with efficiencies of 40%–60%, and are actively being developed for use in clean transportation and renewable energy storage systems. They demonstrate how understanding electrochemistry and the Nernst equation can lead to practical solutions for global energy challenges.

Concentration Cells

When two solutions of different concentrations are mixed, they spontaneously reach an intermediate concentration. A concentration cell operates on the same principle: the half-reactions are identical at both the anode and cathode, but the concentrations in each half-cell differ. The natural drive toward equal concentrations creates a spontaneous redox process, allowing the cell to generate electricity until the concentrations become equal, at which point the cell potential drops to zero.

For example, consider a concentration cell with 0.010 M $\mathrm{AgNO_3}$ in one compartment and 1.0 M $\mathrm{AgNO_3}$ in the other:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\,||\,\mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag\,(s)}$$

At the cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag\,(s)}$$

At the anode:

$$\mathrm{Ag(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-}$$

Overall:

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M)$$

As the cell operates:

- The [$\mathrm{Ag^+}$] increases in the anode compartment as silver oxidizes.
- The [$\mathrm{Ag^+}$] decreases in the cathode compartment as silver deposits on the electrode.
- The total mass of Ag(s) remains constant in the cell, but its distribution changes.

Since the same half-reaction occurs in both compartments, the standard cell potential (E°_{cell}) is zero:

$$E^\circ_{ox} = -E^\circ_{red}$$

To find the cell potential under these conditions, use the Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right) \log \left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

As the reaction proceeds, the concentration difference between the compartments decreases, and so does E_{cell}. When the concentrations become equal, equilibrium is reached, and the cell potential becomes zero ($E_{\text{cell}} = 0$).

Example 11.6.2

Calculate the cell potential in a galvanic cell that has $\mathrm{Mn^{2+}/Mn}$ manganese electrodes in:

- 2.0 M $\mathrm{MnSO_4}$ solution (cathode)
- 5.2 × 10^{-2} M $\mathrm{MnSO_4}$ solution (anode)
- at 25 °C.

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Recognize this as a concentration cell with identical half-reactions but different $\mathrm{Mn^{2+}}$ concentrations.
B. Write the net direction of reaction.
C. Apply the Nernst equation to calculate E_{cell}.

Solution

1. Identify the overall process:
The higher $\mathrm{Mn^{2+}}$ concentration in the cathode compartment drives the spontaneous transfer toward equal concentrations:

$$\mathrm{Mn^{2+}(aq, 2.0\ M)} \rightarrow \mathrm{Mn^{2+}(aq, 5.2 \times 10^{-2}\ M)}$$

2. Determine the number of electrons transferred (n):
For the half-reaction:

$$\mathrm{Mn^{2+} + 2\,e^-} \rightarrow \mathrm{Mn(s)}$$

$n = 2$ electrons.

3. Apply the Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln \frac{[\text{Mn}^{2+}]_{\text{dilute}}}{[\text{Mn}^{2+}]_{\text{concentrated}}}$$

$$E_{\text{cell}} = 0 - \frac{8.314 \frac{\text{J}}{\text{mol K}}(298\ \text{K})}{(2)(96485\ \text{C/mol})}\ln\left(\frac{5.2 \times 10^{-2}}{2.0}\right) = 0.047\ \text{V}$$

Manganese will be oxidized from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

Exercise 11.6.2

What is the cell potential for the following galvanic cell?

$$\text{Pb(s)}\,|\,\text{Pb}^{2+}(aq, 0.025\ M)\,||\,\text{Pb}^{2+}(aq, 2.5\ M)\,|\,\text{Pb(s)}$$

Answer available at the end of this section.

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species when the cell potential and the concentrations of all other species are known. This application explains the widespread use of electrochemical cells in many analytical devices. One of the most common examples is the determination of $[\text{H}^+]$ using a pH meter, as illustrated below.

Example 11.6.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[\text{H}^+]$ in the second compartment is unknown. The shorthand notations for the cell is:

$$\text{Zn(s)}|\text{Zn}^{2+}(\text{aq},\ 1.0\ \text{M})||\text{H}^+(\text{aq},\ ?\ \text{M})|\text{H}_2(\text{g},\ 1.0\ \text{atm})|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Standard Reduction Potentials:

$\text{Zn}^{2+}\,(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Zn}\,(\text{s}) \quad E^\circ_{\text{red}} = -0.76\ \text{V}$

$2\,\text{H}^+\,(\text{aq}) + 2\,\text{e}^- \rightarrow \text{H}_2\,(\text{g}) \quad E^\circ_{\text{red}} = 0.00\ \text{V}$ by definition

Given: cell diagram and standard reduction potentials

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for $[\text{H}^+]$.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq)\ \rightarrow Zn^{2+}\,(aq) + H_2\,(g)} \quad E^\circ_{\text{cell}} = 0.76\ \text{V}$$

$$Q = \frac{P_{\mathrm{H_2}}[\mathrm{Zn^{2+}}]}{[\mathrm{H^+}]^2}$$

B By substituting the given values into the Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

$$0.26\,\text{V} = 0.76\,\text{V} - \frac{(8.314\,\text{J/(mol}\cdot\text{K)})(298\,\text{K})}{(2)(96485\,\text{C/mol})}\ln Q$$

$$\ln Q = 38.94$$

$$Q = e^{38.943} = 8.2 \times 10^{16}$$

$$Q = \frac{P_{\mathrm{H_2}}[\mathrm{Zn^{2+}}]}{[\mathrm{H^+}]^2} = \frac{(1.0)(1.0)}{[\mathrm{H^+}]^2} = 8.2 \times 10^{16}$$

$$[\mathrm{H^+}] = 3.5 \times 10^{-9}\ \text{M}$$

$$pH = -\log(3.5 \times 10^{-9}\ \text{M}) = 8.46$$

The potential of a galvanic cell is used to measure the pH of a solution.

Exercise 11.6.4

Suppose you work for an environmental laboratory and want to use an electrochemical method to measure the concentration of $\mathrm{Pb^{2+}}$ in groundwater. You construct a galvanic cell using a standard oxygen electrode (see reduction reaction below) in one compartment and a lead electrode in a groundwater sample containing acetic acid (to ensure conductivity) in the other. The cell diagram is:

$$\mathrm{Pb\ (s)\ |\ Pb^{2+}\ (aq,\ ?\ M)\ \|\ H^+}(aq, 1.0\ \text{M})\ |\ \mathrm{O_2}(g, 1.0\ atm)\ |\ \mathrm{Pt(s)}$$

When the circuit is closed, the measured potential is 1.62 V. Determine the concentration of $\mathrm{Pb^{2+}}$ in the groundwater.

Standard Reduction Potentials:

$\mathrm{Pb^{2+}\,(aq) + 2\,e^-\ \rightarrow Pb\,(s)} \quad E^\circ_{\text{red}} = -0.13\ \text{V}$

$\mathrm{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^-\ \rightarrow 2\,H_2O\,(l)} \quad E^\circ_{\text{red}} = 1.23\ \text{V}$

Answer available at the end of this section.

Summary

Redox reactions and galvanic cells rarely operate under standard conditions. The Nernst Equation allows us to calculate the voltage of a cell under non-standard conditions, including as concentrations change while a cell operates. These cell potentials can be used to determine the direction of spontaneous reaction for any redox process in aqueous solution.

As a cell operates, reactants are converted to products, so the value of Q increases, the chemical drive for the reaction decreases, and the cell potential decreases:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

At equilibrium, $\Delta G = 0$ and $E_{\text{cell}} = 0$, so $Q = K$.

Concentration cells are a special case where the anode and cathode compartments are identical except for the concentrations. As a concentration cell operates, the concentration difference decreases, and the cell potential drops. When the concentrations become equal (equilibrium), the cell potential becomes zero, and electrical energy can no longer be generated.

Finally, galvanic cells can also be used to determine the concentration of a species when the cell potential and the concentrations of the other species are known, providing a powerful analytical tool for measuring ion concentrations in solution.

Glossary

concentration cell
: A galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute.

fuel cell
: A galvanic cell that continuously converts chemical energy into electrical energy as long as fuel and an oxidant are supplied.

Nernst equation
: An equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials.

Answers

Exercise 11.6.1

1. Find $[\mathrm{OH}^-]$ using pH:

pH = 10.00, so pOH = 14-10.00 = 4.00

$[\mathrm{OH}^-] = 10^{-\mathrm{pOH}} = 1.0 \times 10^{-4}\ \mathrm{M}$

2. Determine the number of electrons transferred by looking at the oxidation states of Mn.

- Mn in $\mathrm{MnO_2}$: +4
- Mn in $\mathrm{MnO_4}^-$: +7

Since the change is +3, 3 electrons are lost per Mn, for a total of 12 electrons.

3. Write the reaction quotient:

$$Q = \frac{[\mathrm{MnO_4}^-]^4}{P_{\mathrm{O_2}}^3[\mathrm{OH}^{-4}]} = \frac{(1.0 \times 10^{-4})^4}{(0.20)^3(1.0 \times 10^{-4})^4} = 1.3 \times 10^2$$

4. Apply the Nernst equation:

$$E_{\text{cell}} = -0.20\,V - \frac{(8.314\,J/(mol \cdot K))(298\,K)}{(12)(96485\,C/mol)}\ln(125) = -0.21\,V$$

The reaction is non-spontaneous under these conditions.

Exercise 11.6.2

1. Identify the overall process:

The higher Pb^{2+} concentration in the cathode compartment drives the spontaneous transfer toward equal concentrations:

$$\mathrm{Pb}^{2+}(\mathrm{aq}, 2.5\ \mathrm{M}) \rightarrow \mathrm{Pb}^{2+}(\mathrm{aq}, 0.025\ \mathrm{M})$$

2. Determine the number of electrons transferred (n):

For the half-reaction:

$$\mathrm{Pb}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Pb}(\mathrm{s})$$

$n = 2$ electrons.

3. Apply the Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln \frac{[\mathrm{Pb}^{2+}]_{\text{dilute}}}{[\mathrm{Pb}^{2+}]_{\text{concentrated}}}$$

$$E_{\text{cell}} = 0 - \frac{8.314\frac{\mathrm{J}}{\mathrm{mol\ K}}(298\ \mathrm{K})}{(2)(96485\ \mathrm{C/mol})}\ln\left(\frac{0.025}{2.5}\right) = 0.059\ \mathrm{V}$$

Exercise 11.6.4

The overall reaction is:

$$2\,\mathrm{Pb}(\mathrm{s}) + \mathrm{O_2}(\mathrm{g}) + 4\,\mathrm{H}^+(\mathrm{aq}) \rightarrow 2\,\mathrm{Pb}^{2+}(\mathrm{aq}) + 2\,\mathrm{H_2O}(\mathrm{l}) \quad E^\circ_{\text{cell}} = 1.36\ \mathrm{V}$$

Reactant quotient:

$$Q = \frac{[\mathrm{Pb}^{2+}]^2}{P_{\mathrm{O_2}}[\mathrm{H}^+]^4}$$

Apply the Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

$$1.62\,\text{V} = 1.36\,\text{V} - \frac{(8.314\,\text{J/(mol}\cdot\text{K))(298\,K)}}{(4)(96485\ \text{C/mol})}\ln Q$$

$$\ln Q = -40.50$$

$$Q = e^{-40.50} = 2.6 \times 10^{-18}$$

$$Q = \frac{[\text{Pb}^{2+}]^2}{P_{\text{O}_2}[\text{H}^+]^4} = \frac{[\text{Pb}^{2+}]^2}{(1.0)(1.0)^4} = 2.6 \times 10^{-18}$$

$$[\text{Pb}^{2+}] = 1.6 \times 10^{-9}\ \text{M}$$

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11.7: Corrosion

Learning Objectives

- Define corrosion and explain why it occurs.
- Describe methods used to prevent or slow corrosion.

Corrosion is the degradation of metals through naturally occurring electrochemical reactions. Examples include rust on iron, tarnish on silver, and the green patina on copper roofs. Corrosion has major economic and environmental impacts: globally, its annual cost exceeds $2 trillion. In Canada, corrosion affects bridges, water systems, and transit vehicles, especially in cities like Toronto, where winter salting and high humidity accelerate damage.

Under normal conditions on Earth, the oxidation of most metals is thermodynamically spontaneous, with notable exceptions like gold and platinum. It is therefore somewhat surprising that metals can be used in our moist, oxygen-rich atmosphere. However, some metals resist corrosion for kinetic reasons: they form thin, stable oxide layers on their surfaces that act as protective barriers, a process called passivation. Aluminum, for example, quickly develops an impermeable oxide coating that protects the metal beneath; aluminum cans also include a plastic lining to prevent acids in beverages from breaching this barrier. Chromium, magnesium, and nickel behave similarly. Stainless steel, an alloy of iron with chromium and often nickel, resists corrosion because chromium forms a protective oxide layer on the surface, protecting the underlying iron.

Chemistry in Everyday Life: Parliament Hill's Green Roofs

If you have visited Ottawa, you have likely seen the green copper roofs of the Parliament Buildings, including the Peace Tower (Figure 11.7.1). These roofs were originally brown when installed in the early 1900s but turned green over time due to corrosion.

The change in colour is a result of oxidation of the copper in air, forming red copper(I) oxide and then black copper(II) oxide:

$$2\,\mathrm{Cu\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{Cu_2\ O\,(s)} \qquad \text{(red)}$$

$$\mathrm{Cu_2O\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CuO\,(s)} \qquad \text{(black)}$$

Air pollution from industrial activity and transportation, including sulfur dioxide from combustion and carbon dioxide and water vapour, further reacted with the copper(II) oxide, forming blue and green copper carbonate and sulfate compounds:

$$2\,\mathrm{CuO\,(s)} + \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \longrightarrow \mathrm{Cu_2CO_3(OH)_2\,(s)} \qquad \text{(green)}$$

$$3\,\mathrm{CuO\,(s)} + 2\,\mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \longrightarrow \mathrm{Cu_3(CO_3)_2(OH)_2\,(s)} \qquad \text{(blue)}$$

$$4\,\mathrm{CuO\,(s)} + \mathrm{SO_3\,(g)} + 3\,\mathrm{H_2O\,(l)} \longrightarrow \mathrm{Cu_4SO_4(OH)_6\,(s)} \qquad \text{(green)}$$

These compounds give the Parliament Buildings their distinctive blue-green patina, which you may have seen on other historic copper roofs. This patina is a passivation layer, like the protective oxide films that form on aluminum and stainless steel, preventing further corrosion of the copper underneath.



Figure 11.7.1:The Parliament Buildings in Ottawa, including the Peace Tower, feature copper roofs that were originally brown when installed but have developed a blue-green patina due to corrosion over time. (Saffron Blaze, CC BY-SA 3.0, via Wikimedia Commons)

Rusting as a Galvanic Cell

In contrast to metals that form protective layers, when iron corrodes, it produces red-brown hydrated iron(III) oxide ($\mathrm{Fe_2O_3 \cdot \mathit{x}\, H_2O}$), known as rust, which does not adhere well to the surface. Instead, rust flakes off, continually exposing fresh iron to air and moisture, allowing corrosion to continue.

Iron rusts only when both oxygen and water are present. For example, an iron nail immersed in deoxygenated water will not rust, even after several weeks. Likewise, a nail submerged in an organic solvent like kerosene will not rust because water is absent, even if oxygen is present.

Rust formation occurs via microscopic galvanic cells that develop on the iron surface (Figure 11.7.2). Iron atoms lose electrons (oxidation) at anodic sites, forming $\mathrm{Fe^{2+}}$ ions, while oxygen is reduced at cathodic sites to form water. Electrons flow through the iron itself from anode to cathode.

The relevant redox reactions under acidic conditions are:
anode (oxidation): $\mathrm{Fe\,(s)} \rightarrow \mathrm{Fe^{2+}\,(aq)} + 2\,\mathrm{e^-} \quad E^\circ_{ox} = 0.45\ \mathrm{V}$

cathode (reduction): $\mathrm{O_2\,(g)} + 4\,\mathrm{H^+\,(aq)} + 4\,\mathrm{e^-} \rightarrow 2\,\mathrm{H_2O\,(l)} \quad E^\circ_{red} = 1.23\ \mathrm{V}$

overall: $2\,\mathrm{Fe\,(s)} + \mathrm{O_2\,(g)} + 4\,\mathrm{H^+\,(aq)} \rightarrow 2\,\mathrm{Fe^{2+}\,(aq)} + 2\,\mathrm{H_2O\,(l)} \quad E^\circ_{cell} = 1.68\ \mathrm{V}$

The large, positive E°_{cell} indicates a strong driving force for the oxidation of iron by $\mathrm{O_2}$ under standard conditions (1 M $\mathrm{H^+}$). Even at pH = 7, the cell potential is highly positive, meaning rusting is still favoured. Atmospheric $\mathrm{CO_2}$ lowers the pH of water (by forming $\mathrm{H^+}$ and $\mathrm{HCO_3^-}$), further enhancing rust formation.

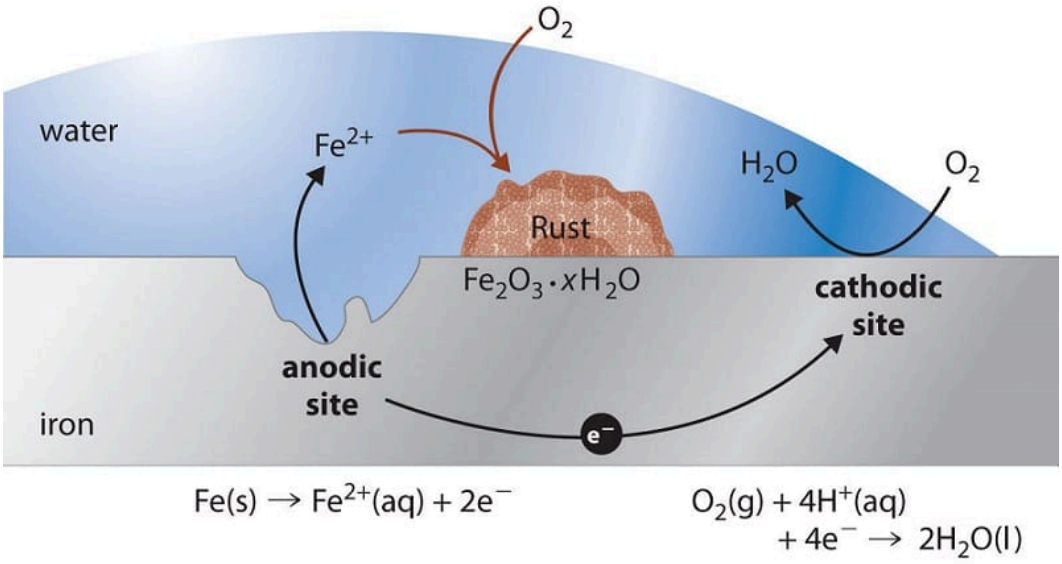


Figure 11.7.2: Rust forms when iron is oxidized to $\mathrm{Fe^{2+}\,(aq)}$ at an anodic sites on the surface, while oxygen is reduced to water on the same iron surface. Electrons are transferred from the anode to the cathode through the iron metal. Water dissolves $\mathrm{Fe^{2+}}$ ions, acting as a salt bridge. The $\mathrm{Fe^{2+}\,(aq)}$ is further oxidized by atmospheric oxygen to form rust ($\mathrm{Fe_2O_3 \cdot \mathit{x}\,H_2O}$). (CC BY-NC-SA; anonymous)

The $\mathrm{Fe^{2+}}$ ions formed are further oxidized by oxygen in the presence of water to form insoluble hydrated iron(III) oxide, known as rust:

$$\mathrm{4\,Fe^{2+}\,(aq) + O_2\,(g) + (4 + 2\,x)\;\; H_2O\,(l) \longrightarrow 2\,Fe_2O_3\;\cdot x\;\; H_2O\,(s) + 8\,H^+\,(aq)}$$

The value of x varies depending on humidity and conditions. Unlike the protective patina on copper, rust does not protect the underlying iron, allowing corrosion to continue as it flakes off and exposes fresh metal to air and moisture.

Prevention of Corrosion

A common way to prevent iron from corroding is to apply a protective paint layer. The paint blocks water and oxygen from reaching the iron surface, preventing the redox reactions needed for rust formation. As long as the paint remains intact, the iron is protected. However, paint can scratch or dent over time, exposing the underlying metal to moisture and oxygen. Because corrosion is electrochemical, two scratches, even far apart, can act as the anode and cathode of a galvanic cell, leading to corrosion and potential mechanical failure (Figure 11.7.3).

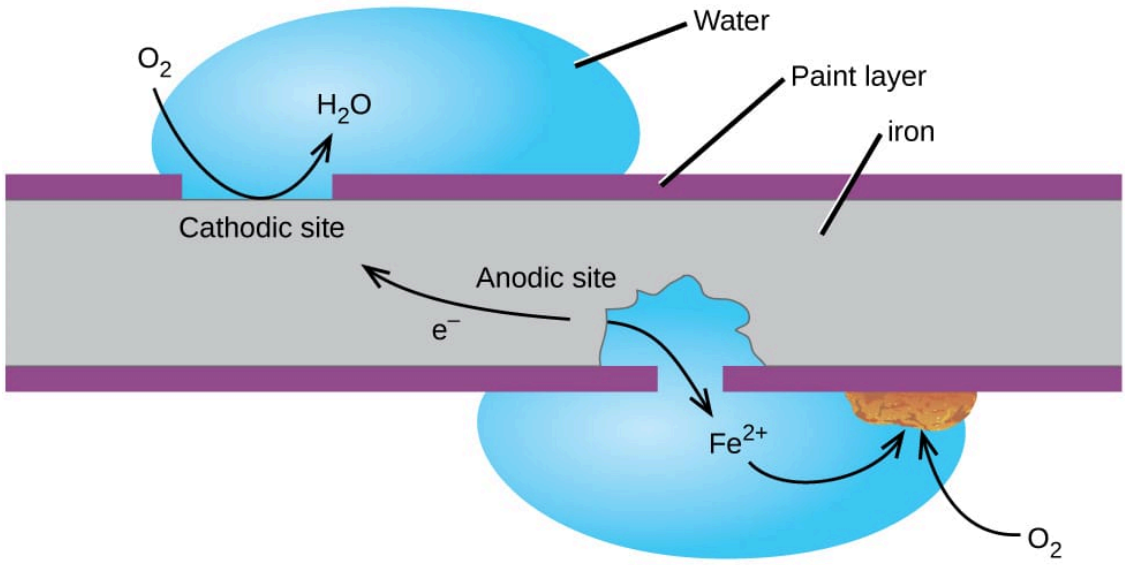


Figure 11.7.3: Corrosion can occur when a painted iron or steel surface is exposed to the environment through a scratch in the paint.

While protective coatings like paint can help prevent corrosion, they can scratch or wear away over time. Another strategy is to use a more easily oxidized metal to protect iron, a method called cathodic protection.

In cathodic protection, a more reactive metal such as zinc (Zn) becomes the anode, while the iron object becomes the cathode. Because of their relative oxidation potentials, Zn oxidizes preferentially, protecting the iron from corrosion.

$$\mathrm{Zn\,(s)} \rightarrow \mathrm{Zn^{2+}\,(aq)} + 2\,\mathrm{e^-} \quad E^\circ_{ox} = 0.76\ \mathrm{V}$$

$$\mathrm{Fe\,(s)} \rightarrow \mathrm{Fe^{2+}\,(aq)} + 2\,\mathrm{e^-} \quad E^\circ_{ox} = 0.45\ \mathrm{V}$$

The reactions that occur in this system are:

$$\underbrace{O_2(g) + 4e^- + 4H^+(aq) \rightarrow 2H_2O(l)}_{\text{reduction at cathode}}$$

$$\underbrace{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-}_{\text{oxidation at anode}}$$

$$\underbrace{2Zn(s) + O_2(g) + 4H^+(aq) \rightarrow 2Zn^{2+}(aq) + 2H_2O(l)}_{\text{overall}}$$

The zinc is gradually oxidized, “sacrificing” itself to protect the iron. For this reason, it is called a sacrificial anode.

Cathodic protection is also the principle underlying galvanized steel, where steel is coated with a thin layer of zinc. Even if the zinc coating is scratched, the zinc continues to protect the steel because it preferentially oxidizes in place of iron. Galvanized steel is widely used in everyday items such as nails, garbage cans, fences, and outdoor structures due to its rust resistance and durability.

A similar corrosion prevention strategy uses sacrificial anodes made of magnesium to protect underground tanks and pipelines (Figure 11.7.4). Replacing these anodes is much more cost-effective than replacing the iron structures they protect.

Magnesium is much more easily oxidized than iron, with:

$$\mathrm{Mg\,(s)} \rightarrow \mathrm{Mg^{2+}\,(aq)} + 2\,\mathrm{e^-} \quad E^\circ_{ox} = 2.37\ \mathrm{V},$$

so it acts as the anode, while the iron pipeline becomes the cathode, preventing the iron from corroding while the magnesium oxidizes.

In this system:

At the anode (Mg): $\mathrm{Mg\,(s)\ \rightarrow Mg^{2+}\,(aq) + 2\,e^-}$

At the cathode (Fe): $\mathrm{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^-\ \rightarrow 2\,H_2O\,(l)}$

Moist soil acts as the electrolyte, allowing ions to move and complete the circuit. As magnesium oxidizes, anions in the soil (e.g., nitrate) migrate toward the anode to balance the positive charge, while cations in the soil (e.g., $\mathrm{H^+}$) move toward the cathode.

In Canada, cathodic protection using sacrificial anodes is widely employed to protect underground pipelines and storage tanks from corrosion, extending the life of critical infrastructure in environments prone to moisture and road salt exposure.

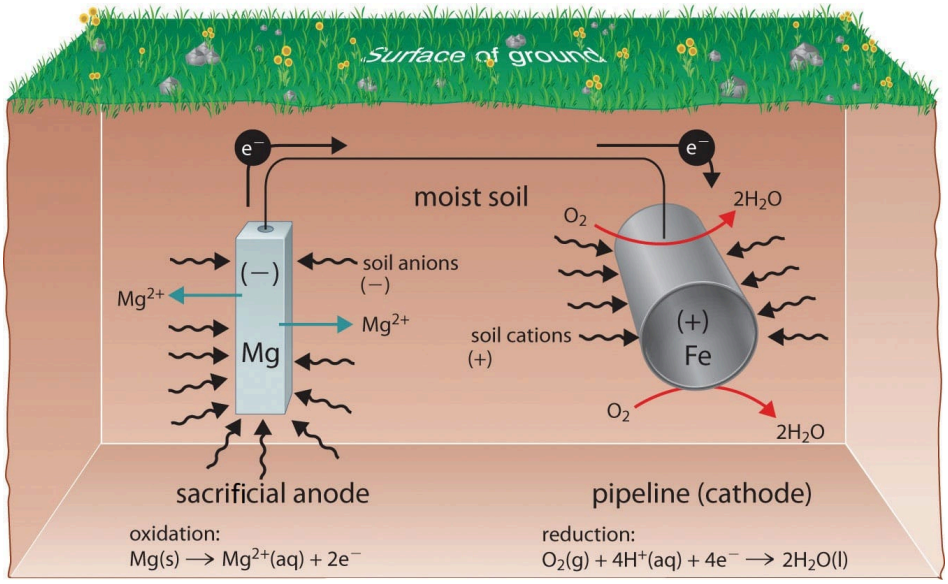


Figure 11.7.4: Connecting a magnesium sacrificial anode to an underground steel pipeline protects it from corrosion.

Example 11.7.1

An old wooden sailboat, held together with iron screws, has a bronze propeller (bronze is an alloy of copper containing about 7%–10% tin).

a) When the boat is immersed in seawater, what corrosion reaction will occur, and what is the standard cell potential (E°_{cell})?

b) How could you prevent this corrosion?

Standard reduction potentials can be found in Table 11.3.1.

Given: identity of metals (iron, copper, tin)

Asked for: corrosion reaction, E°_{cell}, and preventive measures

Solution

a) From Table 11.3.1, the oxidation potentials are found by reversing the reaction and changing the sign:

$\mathrm{Cu\,(s)\ \rightarrow Cu^{2+}\,(aq) + 2\,e^-}\quad E^\circ_{ox} = -0.34\ \mathrm{V}$

$\mathrm{Sn\,(s)\ \rightarrow Sn^{2+}\,(aq) + 2\,e^-}\quad E^\circ_{ox} = 0.14\ \mathrm{V}$

$\mathrm{Fe\,(s)\ \rightarrow Fe^{2+}\,(aq) + 2\,e^-}\quad E^\circ_{ox} = 0.45\ \mathrm{V}$

Copper and tin in bronze have lower oxidation potentials than iron, so they are less likely to oxidize.

Thus:

The iron screws act as the anode and oxidize:

anode: $\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-}$ E°_{ox} = 0.45V

Oxygen in seawater is reduced at the cathode:

cathode: $\mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e^-} \rightarrow 2\,\mathrm{H_2O(l)}$ E°_{red} = 1.23 V

overall: $2\,\mathrm{Fe(s)} + \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} \rightarrow 2\,\mathrm{Fe^{2+}(aq)} + 2\,\mathrm{H_2O(l)}$

Standard cell potential:

E°_{cell} = 1.23 V + 0.45 V = 1.68 V

Conclusion: The iron screws will corrode (oxidize), weakening the boat's structure over time.

b) Possible corrosion prevention strategies (in order of decreasing cost and inconvenience):

1. Replace iron screws with bronze screws
Eliminates the galvanic cell.

2. Store the boat in a dry place
Removes water, preventing corrosion.

3. Attach a zinc sacrificial anode to the propeller shaft
Zinc is more easily oxidized than iron, as indicated by its higher oxidation potential:

$\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-}$ $E^\circ_{ox} = 0.76\ \mathrm{V}$

Therefore, zinc acts as a sacrificial anode, oxidizing in place of the iron screws and protecting them from corrosion.

Practical note: The zinc anode will need periodic replacement (e.g., annually) but is a cost-effective and widely used method in marine environments.



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

Exercise 11.7.1

You want to protect an iron water tank from rusting by using a sacrificial anode. Using the standard reduction potentials below, determine which of the following metals would be suitable.

Metal	Reduction Half-Reaction	E°_{red} (V)
Copper (Cu)	$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$	+0.34
Zinc (Zn)	$\mathrm{Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)}$	-0.76
Magnesium (Mg)	$\mathrm{Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)}$	-2.37
Lead (Pb)	$\mathrm{Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)}$	-0.13
Iron (Fe)	$\mathrm{Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)}$	-0.45

Answer available at the end of this section.

Summary

Corrosion damages metal structures through naturally occurring electrochemical processes.

Iron corrodes in the presence of oxygen and water, and unlike many other metals, the rust that forms does not create a protective layer. Instead, rust flakes off, exposing fresh iron to air and moisture, allowing corrosion to continue.

Corrosion can be prevented by eliminating the factors that promote it. For example, painting a metal surface keeps out water and oxygen, preventing the redox reactions needed for rust formation. Another strategy is to protect iron by using a more reactive metal that oxidizes in place of the iron, a method known as cathodic protection. In this approach, the more active metal serves as a sacrificial anode, gradually oxidizing to protect the iron from corrosion.

Glossary

cathodic protection
: A method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation.

corrosion
: The degradation of metal through an electrochemical process.

Answers

Exercise 11.7.1

To protect iron using a sacrificial anode, the anode metal must oxidize more easily than iron. This means the metal itself must have a stronger tendency to lose electrons (oxidize) than iron. Since standard tables list reduction potentials for the metal ions, a lower (more negative) reduction potential for the ion means the metal is more easily oxidized.

Therefore, to choose a suitable sacrificial anode:

- Compare the reduction potential of the metal ions to that of $\mathrm{Fe^{2+}}$
- Metals whose ions have lower (more negative) reduction potentials than iron will oxidize preferentially, sacrificing themselves to protect the iron.

Zinc (Zn) and Magnesium (Mg) would be suitable sacrificial anodes.

Copper and lead will not oxidize before iron and are unsuitable as sacrificial anodes.

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11.8: Electrolysis

Learning Objectives

- Describe how electrolysis uses electricity to drive nonspontaneous redox reactions.
- Compare the operation of electrolytic and galvanic cells.
- Calculate the mass of substances deposited or consumed during electrolysis using current and time.

So far in this chapter, we have discussed galvanic cells, in which spontaneous redox reactions produce electrical energy. In these cells, a redox system does work on its surroundings as electrons produced by the redox reaction flow through an external circuit.

In this final section, we will examine the reverse scenario: using electrical energy to drive a nonspontaneous redox reaction. This process, called electrolysis, occurs when an external voltage is applied that is large enough to drive a nonspontaneous redox reaction.

Both galvanic and electrolytic cells contain two electrodes (solid metals) connected to an external circuit, providing a path for electron transfer (Figure $11.8.1$). Oxidation always occurs at the anode and reduction at the cathode, regardless of whether the cell is galvanic or electrolytic. When the circuit is closed, electrons always flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality.

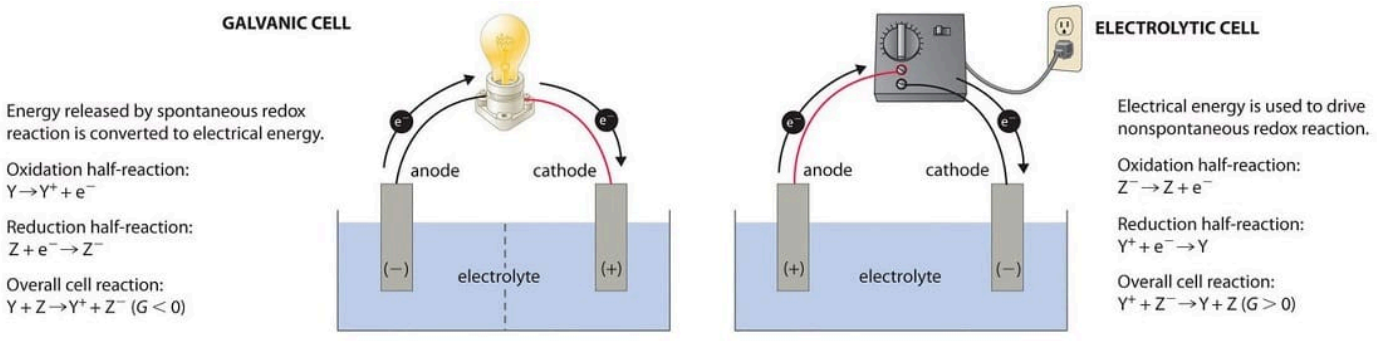


Figure $11.8.1$: Electrochemical Cells. A galvanic cell (left) converts the energy from a spontaneous redox reaction into electrical energy. Oxidation and reduction usually occur in separate compartments, connected by an external electrical circuit and by a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier). The potential difference between the electrodes causes electrons to flow through the circuit, generating an electric current.

In an electrolytic cell (right), an external power source supplies electrical energy, generating a potential difference that forces electrons to flow and drives a nonspontaneous redox reaction. Most electrolytic cells use a single compartment.

A familiar example of electrolysis is recharging a battery, where an external power source forces the discharge reaction to run in reverse, partially restoring the cell composition and voltage. Electrolysis is also used in metal refining, the production of commodity chemicals, and electroplating (coating objects with a thin metal layer, as in jewelry, utensils, and automotive parts).

To illustrate the essential concepts of electrolysis, we will examine a few specific examples.

Electrolysis of Molten Sodium Chloride

Metallic sodium (Na) and chlorine gas $(\mathrm{Cl_2})$ are used in many applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, $\mathrm{NaCl\,(l)}$. This process typically uses a Downs cell, as shown in the simplified illustration in

Figure 11.8.2. The reactions are:

$$\begin{array}{lll} \text{anode:} & 2\,Cl^-\,(l) \rightarrow Cl_2\,(g) + 2\,e^- & E^\circ_{ox} = -1.36\,V \\ \text{cathode:} & Na^+\,(l) + e^- \rightarrow Na\,(l) & E^\circ_{red} = -2.71\,V \\ \text{overall:} & 2\,Na^+\,(l) + 2\,Cl^-\,(l) \rightarrow 2\,Na\,(l) + Cl_2\,(g) & E^\circ_{cell} = -4.07\,V \end{array}$$

The cell potential for this process is negative, indicating that the reaction is not spontaneous under standard state conditions. The power supply (battery) must supply a minimum of 4.07 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

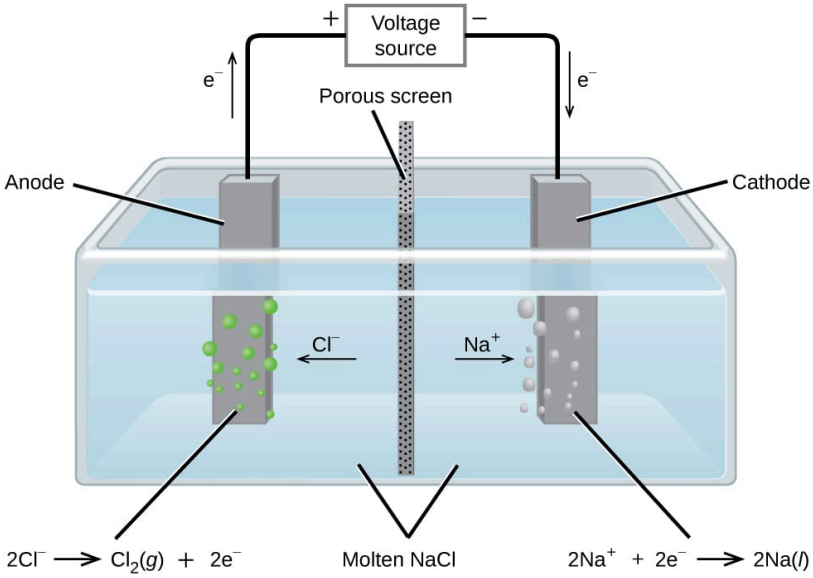


Figure 11.8.2: Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent them from recombining to form sodium chloride again.

Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas using electrolysis. To improve electrical conductivity without introducing a different redox species, a strong acid is typically added to increase the hydrogen ion concentration.

The redox processes associated with this cell are:

$$\begin{array}{lll} \text{oxidation:} & 2\,H_2O\,(l) \rightarrow O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- & E^\circ_{ox} = -1.23\,V \\ \text{reduction:} & 2\,H^+\,(aq) + 2\,e^- \rightarrow H_2\,(g) & E^\circ_{red} = 0\,V \\ \text{overall:} & 2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g) & E^\circ_{cell} = -1.23\,V \end{array}$$

Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by applying a voltage greater than +1.23 V. Keep in mind that these standard electrode potentials are used to inform thermodynamic predictions, but the cell is not operating under standard state conditions. Therefore, the calculated cell potential represents an approximate value rather than an exact voltage.

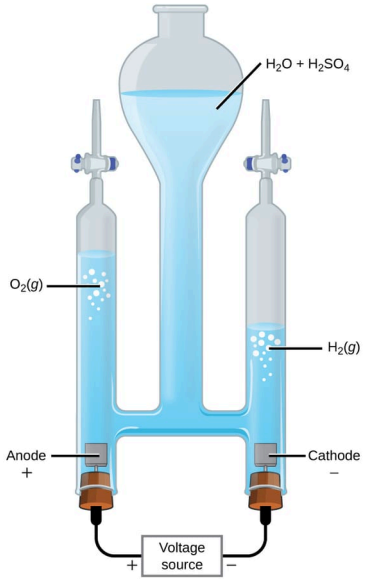


Figure 11.8.3: The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen gas at the cathode.

Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is more complicated than the electrolysis of molten salts because multiple species can be oxidized and reduced.

Anode reactions:

First, consider the anode. The possible oxidation reactions are:

$$\begin{aligned} &\text{(i)}\ 2\,\mathrm{Cl^-}(aq) \rightarrow \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} && E^\circ_{\text{ox}} = -1.358\ \mathrm{V} \\ &\text{(ii)}\ 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{O_2}(g) + 4\,\mathrm{H^+}(aq) + 4\,\mathrm{e^-} && E^\circ_{\text{ox}} = -1.229\ \mathrm{V} \end{aligned}$$

These standard potentials suggest that water should be oxidized at the anode because it requires a less negative potential (–1.229 V vs. –1.358 V for chloride ions). However, when the experiment is run, chlorine gas, not oxygen, is produced at the anode. This discrepancy is due to a concept called overpotential, which is the extra voltage beyond the theoretical potential that must be applied to make a reaction occur at a practical rate. Overpotential arises from kinetic barriers such as reaction mechanisms, electrode surface properties, and gas bubble formation, which can slow reactions even when thermodynamically favourable.

The detailed study of overpotential is beyond the scope of CHM 135H, but it is important to be aware that it can affect which reactions actually occur during electrolysis. In this case, the overpotential for producing oxygen gas is high enough that chloride ions are oxidized more easily under typical conditions. As a result, chlorine gas forms at the anode during the electrolysis of aqueous sodium chloride.

Cathode reactions:

Now consider the cathode. Three reductions could occur:

$$\begin{aligned} &\text{(iii)}\ 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \rightarrow \mathrm{H_2}(g) && E^\circ_{\text{red}} = 0.000\ \mathrm{V} \\ &\text{(iv)}\ 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e^-} \rightarrow \mathrm{H_2}(g) + 2\,\mathrm{OH^-}(aq) && E^\circ_{\text{red}} = -0.828\ \mathrm{V} \\ &\text{(v)}\ \mathrm{Na^+}(aq) + \mathrm{e^-} \rightarrow \mathrm{Na}(s) && E^\circ_{\text{red}} = -2.71\ \mathrm{V} \end{aligned}$$

Reduction of sodium ions (v) is ruled out because it requires a highly negative potential. Under standard conditions, the reduction of hydrogen ions (iii) would be favoured over water reduction (iv). However, in a neutral sodium chloride solution (pH 7), the hydrogen ion concentration is only 1×10^{-7} M, making reaction (iii) infrequent. Thus, water is reduced at the cathode, producing hydrogen gas and hydroxide ions (reaction iv).

Overall cell reaction:

$$\text{overall: } 2\,H_2O(l)+2\,Cl^-(aq) \rightarrow H_2(g) + Cl_2(g)+2\,OH^-(aq) \quad E^\circ_{cell} = -2.186\ V$$

As electrolysis proceeds, hydroxide ions replace chloride ions in solution. By evaporating the water after electrolysis, sodium hydroxide can be collected. Sodium hydroxide is a valuable industrial product used in oven cleaners, drain openers, and in the production of paper, fabrics, and soap.

Electroplating

An important use of electrolytic cells is electroplating, which deposits a thin coating of one metal onto a conducting surface. Electroplating can make an object more corrosion-resistant, strengthen its surface, improve its appearance, or purify a metal. Common electroplating metals include cadmium, chromium, copper, gold, nickel, silver, and tin. Consumer products that often use electroplating include silver- or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can see how electroplating works by looking at the production of silver-plated tableware (Figure 11.8.4).

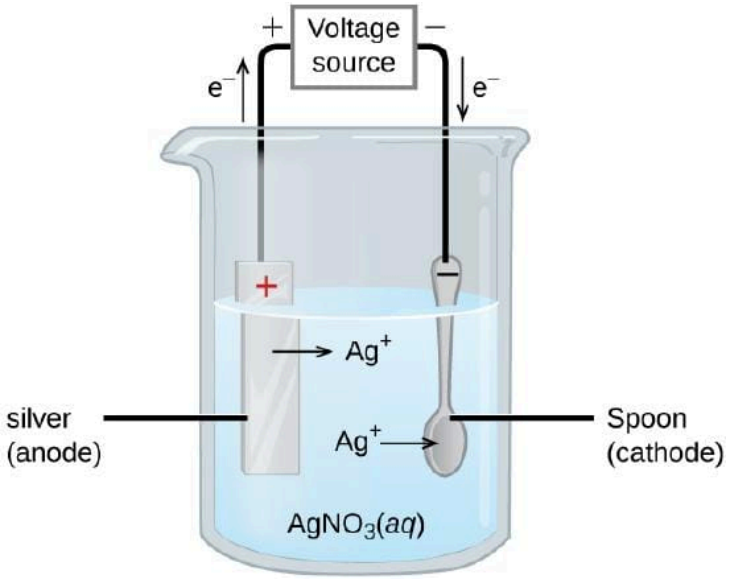


Figure 11.8.4: The spoon, made of an inexpensive metal, is connected to the negative terminal of a voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current passes through the solution, silver metal is removed from the anode and deposited on the cathode.

In the figure, the anode (left) is a silver electrode, and the cathode (right) is the spoon. Both electrodes are immersed in a silver nitrate ($AgNO_3$) solution. When the potential is applied and current flows, silver metal is oxidized at the anode:
anode: $Ag\,(s) \rightarrow Ag^+\,(aq) + e^-$

At the cathode, silver ions from the solution gain electrons and are deposited onto the spoon:
cathode: $Ag^+\,(aq) + e^- \rightarrow Ag\,(s)$

The net result is the transfer of silver metal from the anode to the cathode, building up a thin, even layer of silver on the surface of the spoon. The quality of electroplating is determined by the thickness and uniformity of the deposited layer, which depend on the current and the time the object is plated.

Chemistry in Everyday Life: Rechargeable Batteries

Lithium ion batteries (Figure 11.8.5) power many of the devices we use every day, from phones to laptops and electric vehicles. These batteries are popular because they are lightweight, deliver high current, provide a nearly constant voltage during discharge, and retain their charge well during storage.

During discharge, lithium ions move from the graphite anode (negative electrode) to the metal oxide cathode (positive electrode), providing electrical energy. When the battery is charged, an external power source forces the lithium ions back into the graphite anode, storing energy for later use.

The cell reactions during discharge are:

$$\begin{aligned}
&\text{anode:} && \mathrm{Li}_x\mathrm{C}_6 \rightarrow \mathrm{x\ Li^+ + x\ e^- + C_6\,(s)} \\
&\text{cathode:} && \mathrm{Li_{1-x}CoO_2\,(s) + x\ Li^+ + x\ e^- \rightarrow LiCoO_2} \\
&\text{cell:} && \mathrm{Li_{1-x}CoO_2\,(s) + Li_xC_6 \rightarrow LiCoO_2 + C_6\,(s)} \qquad E_{\text{cell}} \approx +3.7\,\text{V}
\end{aligned}$$

In this notation, x represents the fraction of lithium ions that move during charging and discharging. The ability of lithium ions to move reversibly between the two electrodes allows lithium-ion batteries to store and deliver energy efficiently.

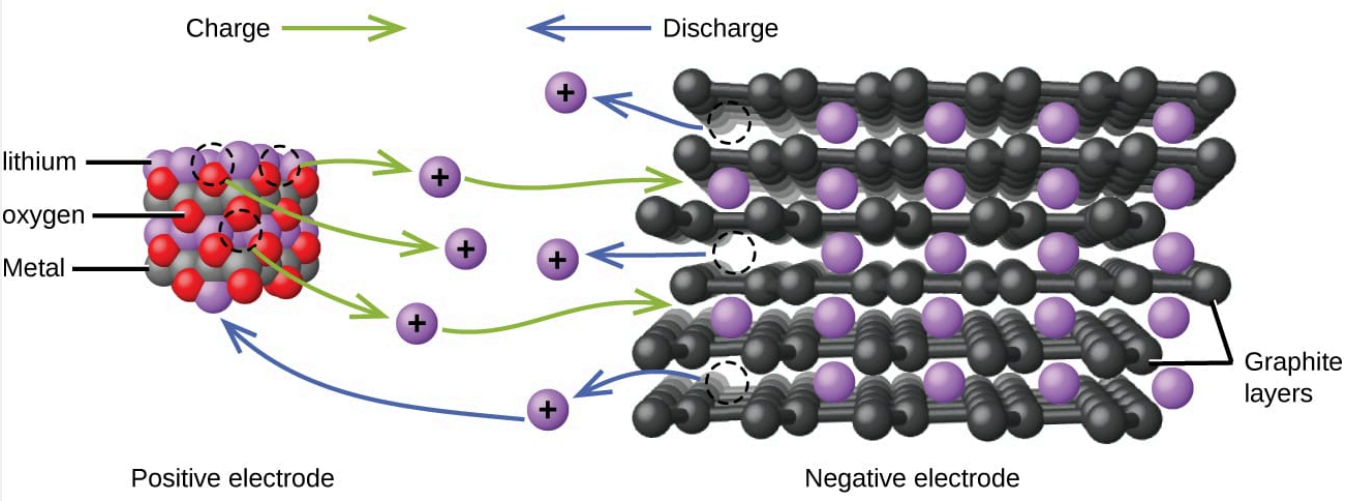


Figure 11.8.5: During discharge, lithium ions move from the anode to the cathode, powering devices. When charging, the ions return to the anode, storing energy for later use.

Lead-acid batteries (Figure 11.8.6) are among the oldest rechargeable batteries and are widely used in cars to power starter motors, lights, and electronics. They are valued for their ability to deliver a high current quickly and their low cost, despite being heavy and containing a corrosive sulfuric acid electrolyte. Each lead-acid cell provides about 2 V, and six cells are connected in series to form a 12-V car battery. The reactions in a lead-acid battery are:

$$\begin{aligned}
&\text{anode:} && \mathrm{Pb\,(s) + HSO_4^-\,(aq) \rightarrow PbSO_4\,(s) + H^+\,(aq) + 2\,e^-} \\
&\text{cathode:} && \mathrm{PbO_2\,(s) + HSO_4^-\,(aq) + 3\,H^+\,(aq) + 2\,e^- \rightarrow PbSO_4\,(s) + 2\,H_2O\,(l)} \\
&\text{cell:} && \mathrm{Pb\,(s) + PbO_2\,(s) + 2\,H_2SO_4\,(aq) \rightarrow 2\,PbSO_4\,(s) + 2\,H_2O\,(l)} \qquad E_{\text{cell}} \approx +2\,\text{V}
\end{aligned}$$

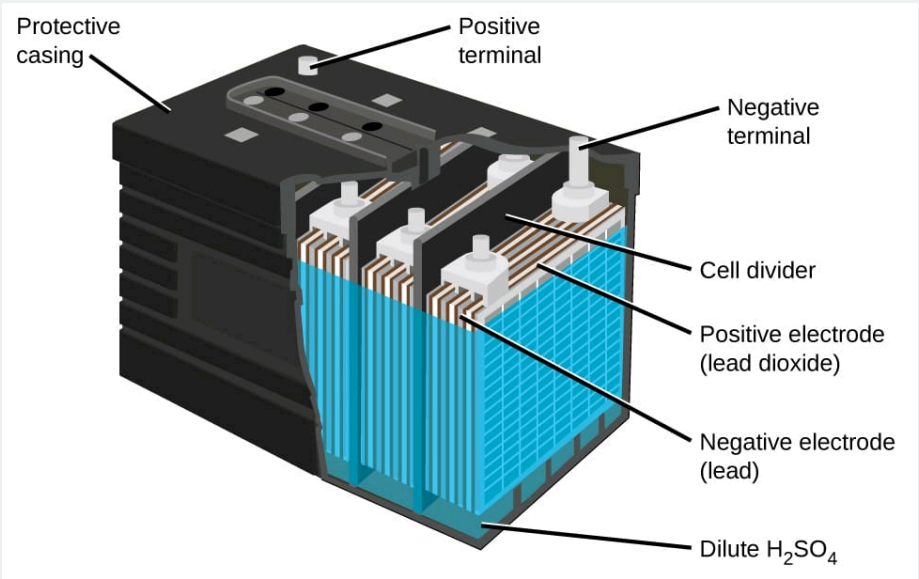


Figure 11.8.6: The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

While lead-acid batteries are reliable and easily rechargeable, they contain a significant amount of lead and must be disposed of properly to prevent environmental contamination.

These examples illustrate how electrolysis and redox chemistry power the batteries in our everyday lives, providing the energy to start cars, run devices, and store renewable energy.

Quantitative Aspects of Electrolysis

Electrical current is defined as the rate of flow of charge. In the context of electrolysis, this usually refers to the flow of electrons through an external circuit. Current is measured in amperes (A), where:

$$1A = 1C/s$$

meaning that one ampere corresponds to one coulomb of charge passing a point per second.

The total charge transferred, Q, when a constant current, I, flows for a time interval, t, is given by:

$$Q = It$$

When electrons are transferred during a redox process, the stoichiometry of the reaction can be used to determine the total charge involved. For example, in the generic reduction process:

$$\mathrm{M}^{n+}\,(\mathrm{aq}) + \mathrm{n\ e}^{-} \rightarrow \mathrm{M}\,(\mathrm{s})$$

n electrons are transferred for each M^{n+} reduced. The total charge transferred is therefore:

$$Q = moles(e^{-}) \times F$$

where F is Faraday's constant, the charge carried by one mole of electrons (F = 96,485 C/mol).

When electrolysis occurs in an electrochemical cell, current can be measured directly and used in stoichiometric calculations related to the cell's redox reaction. By combining $Q = It$ and $Q = moles(e^{-}) \times F$, you can determine the amount of substance produced or consumed during electrolysis based on the current and time the current is applied.

Example 11.8.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for 1 hour (3600 s). How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Calculate the total charge transferred:

$$Q = It = (10.23\frac{C}{s})(3600\ s) = 3.683 \times 10^{4}\ C$$

Calculate moles of electrons using Faraday's constant:

$$Q = moles(e^{-}) \times F \ \Rightarrow\ moles(e^{-}) = \frac{Q}{F} = \frac{3.683 \times 10^{4}\,\mathrm{C}}{96485\,\mathrm{C/mol}} = 0.3817\,\mathrm{mol}$$

Determine mass of silver deposited:

From cathode half-reaction:

$$\mathrm{Ag}^{+}\,(\mathrm{aq}) + \mathrm{e}^{-} \rightarrow \mathrm{Ag}\,(\mathrm{s})$$

1 mol of electrons deposits 1 mol of Ag.

Using the molar mass of silver (107.9 g/mol):

$$\text{mass } Ag = 0.3817\,\text{mol e}^- \times \frac{1\,\text{mol Ag}}{1\,\text{mol e}^-} \times \frac{107.9\,\text{g Ag}}{1\,\text{mol Ag}} = 41.19\,\text{g Ag}$$

Exercise 11.8.1

Aluminum metal can be made from aluminum(III) ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 25.0 A passed through the solution for 15.0 minutes?

Answer available at the end of this section.

Summary

An electrolytic cell uses electrical energy to drive a nonspontaneous redox reaction. Oxidation occurs at the anode and reduction at the cathode.

When more than one product is possible at an electrode, the substance that is more easily oxidized forms at the anode, while the substance that is more easily reduced forms at the cathode. However, in some cases, the predicted product does not form due to overpotential (overvoltage), which is the additional voltage required to drive a reaction at a practical rate.

Electroplating uses electrolysis to deposit a thin layer of metal onto a conducting surface, improving corrosion resistance, appearance, or strength.

The quantitative aspects of electrolysis can be summarized using the relationships:
$Q = I \times t$ and $Q = moles(e^-) \times F$

where:

Q = total charge transferred (C),

I = current (A),

t = time (s),

moles (e^-) = actual amount of moles of electrons transferred,

F = Faraday's constant (96,485 C/mol).

These relationships allow the calculation of the mass of a substance produced or consumed during electrolysis based on the measured current and the time the current is applied.

In all electrolytic cells, the key distinction from galvanic cells is that an external power source must supply energy to drive the redox reaction, as it is not thermodynamically spontaneous.

Glossary

current
: The flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes.

electrolysis
: A process that uses electrical energy to drive a nonspontaneous redox reaction.

electrolytic cell
: An electrochemical cell with two electrodes in a single compartment where an external power source supplies electrical energy, generating a potential difference that forces electrons to flow and drives a nonspontaneous redox reaction.

electroplating
Coating objects with a thin metal layer via electrolysis.

overpotential
The the extra voltage beyond the theoretical potential that is required to make a reaction occur at a practical rate.

Answers

Exercise 11.8.1

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$$

$$(25.0\text{ C/s})(15.0\text{ min})\left(\frac{60\text{ s}}{\text{min}}\right)\left(\frac{mol\ e^-}{96485\text{ C}}\right)\left(\frac{1\ mol\ Al}{3\ mol\ e^-}\right)\left(\frac{26.98\text{ g}}{mol}\right) = 2.10\text{ g Al}$$

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11.E: Electrochemistry (Exercises)

Redox reactions

Exercise 11.E.1*

What do oxidation and reduction mean in terms of electron transfer?

How does each process change the oxidation number of an element?

Can oxidation or reduction happen alone?

Answer available at the end of this section.

Exercise 11.E.2*

Consider the following redox reaction in acidic solution:

$$\mathrm{MnO_4^-\,(aq) + 5\,Fe^{2+}\,(aq) + 8\,H^+\,(aq) \rightarrow Mn^{2+}\,(aq) + 5\,Fe^{3+}\,(aq) + 4\,H_2O\,(l)}$$

a) Identify which species is oxidized and which is reduced.

b) Identify the oxidizing agent and the reducing agent.

c) Write the oxidation half-reaction and the reduction half-reaction for this process.

Answer available at the end of this section.

Exercise 11.E.3*

Consider the following redox reaction in basic solution:

$$\mathrm{Zn\,(s) + 4\,OH^-\,(aq) + Br_2\,(l) \rightarrow Zn(OH)_4^{2-}\,(aq) + 2\,Br^-\,(aq)}$$

a) Identify which species is oxidized and which is reduced.

b) Identify the oxidizing agent and the reducing agent.

c) Write the oxidation half-reaction and the reduction half-reaction for this process.

Answer available at the end of this section.

Exercise 11.E.4**

Balance the following redox reactions in acidic solution.

a) $\mathrm{Cu\,(s) + NO_3^-\,(aq) \rightarrow Cu^{2+}\,(aq) + NO\,(g)}$

b) $\mathrm{Cr_2O_7^{2-}\,(aq) + Ni\,(s) \rightarrow Cr^{3+}\,(aq) + Ni^{2+}\,(aq)}$

c) $\mathrm{MnO_4^-\,(aq) + C_2O_4^{2-}\,(aq) \rightarrow CO_2\,(g) + Mn^{2+}\,(aq)}$

Answer available at the end of this section.

Exercise 11.E.5***

Balance the following redox reactions in basic solution.

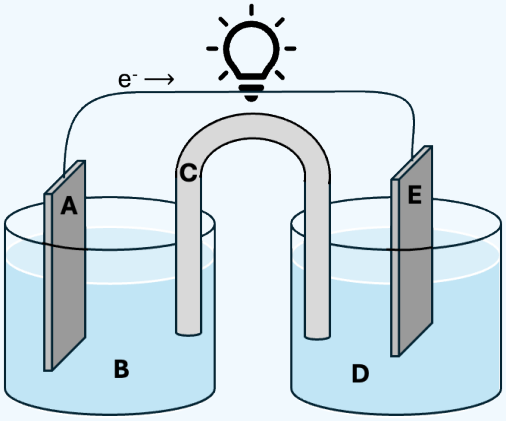
a) $\mathrm{MnO_4^-\,(aq) + IO_3^-\,(aq) \longrightarrow IO_4^- + MnO_2\,(s)}$

b) $\mathrm{Cr(OH)_4^-\,(aq) + ClO^-\,(aq) \longrightarrow CrO_4^{2-}\,(aq) + Cl_2\,(g)}$

Answer available at the end of this section.

Galvanic Cells

Exercise 11.E.6*



Consider the diagram of the galvanic cell:

Identify the following:

a) Anode

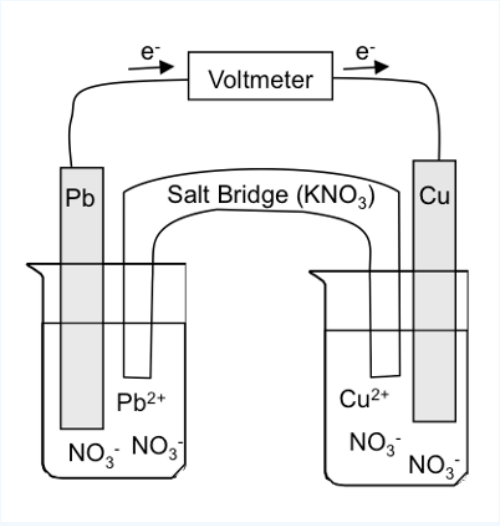
b) Cathode

c) Salt bridge

d) Electrode with a negative charge

Answer available at the end of this section.

Exercise 11.E.7**



Consider the diagram of the galvanic cell:

a) What metal makes up the anode?

b) What metal makes up the cathode?

c) Which electrode has a positive charge?

d) Write the two half-reactions that occur in this galvanic cell. What is the overall balanced cell reaction?

e) Which electrode loses mass as the cell operates?

f) Which electrode could be replaced with an inactive material, such as platinum?

g) Write the shorthand notation for this galvanic cell.

Answer available at the end of this section.

Exercise $11.E.8$**

A galvanic cell is constructed using a $\mathrm{Ag/Ag^+}$ half-cell and a $\mathrm{Cu/Cu^{2+}}$ half-cell. The copper electrode is negative.

a) Write the oxidation half-reaction, the reduction half-reaction, and the overall balanced redox reaction for this galvanic cell.

b) Draw and label the galvanic cell, indicating:

- the anode and cathode,
- the charge on each electrode,
- the direction of electron flow in the external circuit,
- the salt bridge, containing $\mathrm{KNO_3}$ and the direction of ion flow.

Answer available at the end of this section.

Exercise $11.E.9$**

Write cell shorthand notations for the following cell reactions, using platinum as an inert electrode as needed.

a) $\mathrm{Mg\,(s) + Ni^{2+}\,(aq) \rightarrow Mg^{2+}\,(aq) + Ni\,(s)}$

b) $\mathrm{2\,Ag^{+}\,(aq) + Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2\,Ag\,(s)}$

c) $\mathrm{Mn\,(s) + Sn^{2+}\,(aq) \rightarrow Mn^{2+}\,(aq) + Sn\,(s)}$

d. $\mathrm{3\,Cu^{+}\,(aq) + Au^{3+} \rightarrow 3\,Cu^{2+}\,(aq) + Au\,(s)}$

Answer available at the end of this section.

Exercise $11.E.10$*

Why is a salt bridge necessary in galvanic cells?

Answer available at the end of this section.

Standard Reduction Potentials (E°_{cell})

Exercise $11.E.11$*

What does the standard cell potential (E°_{cell}) tell us about a galvanic cell and the redox reaction occurring within it?

Answer available at the end of this section.

Exercise $11.E.12$*

For each of the following reactions:

- Identify which half-reaction occurs at the cathode and which occurs at the anode.
- Balance the overall redox reaction if needed.

- Calculate the standard cell potential (E°_{cell}) for the reaction.

a) $\mathrm{Fe^{3+}\,(aq) + Zn\,(s) \rightarrow Fe^{2+}\,(aq) + Zn^{2+}\,(aq)}$

b) $\mathrm{Cu^{2+}\,(aq) + Zn\,(s) \rightarrow Cu\,(s) + Zn^{2+}\,(aq)}$

c) $\mathrm{Cd\,(s) + Cu^{2+}\,(aq) \rightarrow Cd^{2+}\,(aq) + Cu\,(s)}$

d) $\mathrm{Fe^{2+}\,(aq) + Cl_2\,(g) \rightarrow Fe^{3+}\,(aq) + 2\,Cl^-\,(aq)}$

Standard reduction potentials can be found in Table 11.3.1.

Answer available at the end of this section.

Exercise 11.E.13**

Balance the following redox reaction under acidic conditions:

$$\mathrm{Mn^{2+}\,(aq) + Cl_2\,(g) \rightarrow MnO_4{}^-\,(aq) + 2\,Cl^-\,(aq)}$$

Is the reaction spontaneous under standard state conditions?

Standard reduction potentials can be found in Table 11.3.1.

Answer available at the end of this section.

Exercise 11.E.14**

Consider the following reduction potentials:

$\mathrm{Ca^{2+}\,(aq) + 2\,e^- \longrightarrow Ca\,(s)} \quad E^\circ_{red} = -2.87\ V$

$\mathrm{Cd^{2+}\,(aq) + 2\,e^- \longrightarrow Cd\,(s)} \quad E^\circ_{red} = -0.40\ V$

$\mathrm{Fe^{3+}\,(aq) + e^- \longrightarrow Fe^{2+}\,(aq)} \quad E^\circ_{red} = +0.77\ V$

$\mathrm{Ag^{+}\,(aq) + e^- \longrightarrow Ag\,(s)} \quad E^\circ_{red} = +0.80\ V$

Which of these species is the strongest oxidizing agent? Which species is the strongest reducing agent?

Answer available at the end of this section.

Exercise 11.E.15***

Consider the following reduction potentials:

$\mathrm{S_2O_8{}^{2-}\,(aq) + 2\,e^- \longrightarrow 2\,SO_4{}^{2-}\,(aq)} \quad E^\circ_{red} = 2.01\ V$

$\mathrm{Sn^{2+}\,(aq) + 2\,e^- \longrightarrow Sn\,(s)} \quad E^\circ_{red} = -0.14\ V$

$\mathrm{Fe^{2+}\,(aq) + 2\,e^- \longrightarrow Fe\,(s)} \quad E^\circ_{red} = -0.45\ V$

a) Which species is the strongest oxidizing agent? Which species is the strongest reducing agent?

b) Using these half-reactions, write three spontaneous redox reactions (under standard state conditions) and calculate (E°_{cell}) for each.

Answer available at the end of this section.

Cell Potentials, Free Energy, and Equilibrium

Exercise 11.E.16*

Calculate ΔG° for the reactions below.

a) $\mathrm{Cu\,(s) + Sn^{4+}\,(aq) \rightarrow Cu^{2+}\,(aq) + Sn^{2+}\,(aq)}$

b) $\mathrm{2\,Cl_2\,(g) + 2\,H_2O\,(l) \rightarrow O_2\,(g) + 4\,H^+\,(aq) + 4\,Cl^-\,(aq)}$

Standard reduction potentials can be found in Table 11.3.1.

Answer available at the end of this section.

Exercise 11.E.17*

Calculate the equilibrium constant (K) for the following reactions.

a. $\mathrm{Ca^{2+}\,(aq) + 2\,Li\,(s) \rightleftharpoons Ca\,(s) + 2\,Li^+\,(aq)}$
b. $\mathrm{Cu^{2+}\,(aq) + Ni(OH)_2\,(s) + 2\,OH^-\,(aq) \rightleftharpoons Cu\,(s) + NiO_2\,(s) + 2\,H_2O\,(l)}$

Standard reduction potentials can be found in Table 11.3.1.

Answer available at the end of this section.

Exercise 11.E.18*

At 298 K, the following reaction has an equilibrium constant of 2.32 x 10^{27}.

$\mathrm{6\,Br^-\,(aq) + 14\,H^+\,(aq) + Cr_2O_7^{2-}\,(aq) \rightleftharpoons 2\,Cr^{3+}\,(aq) + 3\,Br_2\,(l) + 7\,H_2O\,(l)}$

What is the standard cell potential for the reaction? What is the standard free energy change?

Answer available at the end of this section.

Cell Potentials Beyond Standard Conditions

Exercise 11.E.19**

Consider the following reaction taking place in a galvanic cell at 298 K:

$\mathrm{Cu^{2+}\,(aq) + Zn\,(s) \rightarrow Cu\,(s) + Zn^{2+}\,(aq)}$

reduction (cathode):$\mathrm{Cu^{2+}\,(aq) + 2\,e^- \rightarrow Cu\,(s)}$ $\quad E^\circ_{red} = 0.34\ \mathrm{V}$

oxidation (anode):$\mathrm{Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2\,e^-}$ $\quad E^\circ_{ox} = 0.76\ \mathrm{V}$

a) What is the standard cell potential (E°_{cell})?

b) What is the cell potential (E_{cell}) when [Cu^{2+}] = 1.5 M and [Zn^{2+}]= 0.10 M? (Before performing the calculation, would you expect the cell potential to be greater or less than the standard cell potential?)

c) What is the cell potential (E_{cell}) when [Cu^{2+}] = 0.50 M and [Zn^{2+}]= 1.5 M? (Before performing the calculation, would you expect the cell potential to be greater or less than the standard cell potential?)

Answer available at the end of this section.

Exercise 11.E.20**

The following galvanic cell has a cell potential (E_{cell}) of 1.54 V. What is the concentration of Ag^+ in the cell?

$$Zn\,(s)\ |\ Zn^{2+}(2.00\ M)||\ Ag^+(?\,M)\ |\ Ag\,(s)$$

Standard reduction potentials:

$Zn^{2+}\,(aq) + 2\,e^-\ \rightleftharpoons Zn\,(s) \quad E^\circ_{red} = -0.76\ V$
$Ag^+\,(aq) + e^-\ \rightleftharpoons Ag\,(s) \quad E^\circ_{red} = 0.80\ V$

Answer available at the end of this section.

Exercise 11.E.21**

What is the cell potential (E_{cell}) for the following galvanic cell?

$Co\,(s)\ |\ Co^{2+}(0.6\ M)||\ Fe^{3+}\ (1.0\ M),\ Fe^{2+}(0.9\ M)|\ Pt\,(s)$

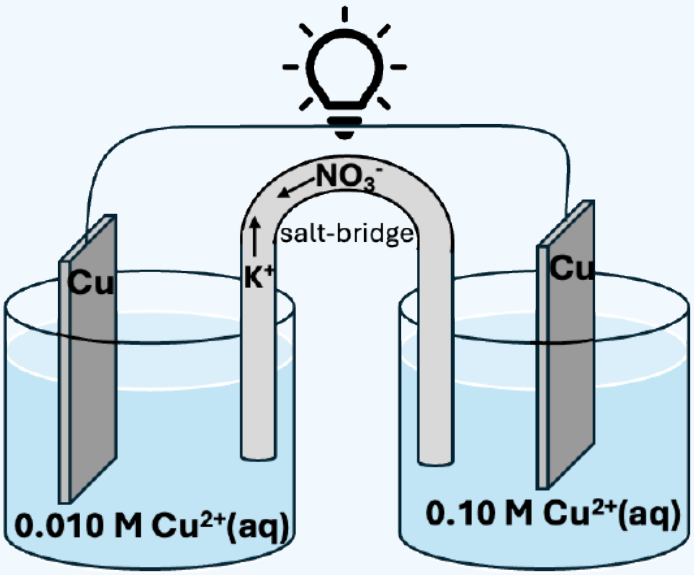
Standard reduction potentials:

$Co^{2+}\,(aq) + 2\,e^-\ \rightleftharpoons Co\,(s) \quad E^\circ_{red} = -0.28\ V$
$Fe^{3+}\,(aq) + e^-\ \rightleftharpoons Fe^{2+}\,(aq) \quad E^\circ_{red} = 0.77\ V$

Answer available at the end of this section.

Exercise 11.E.22**

What is the cell potential (E_{cell}) for the following concentration cell?



Answer available at the end of this section.

Exercise 11.E.23***

For the following redox reaction:

$\mathrm{Co(s) + Ni^{2+}(aq) \rightleftharpoons Ni(s) + Co^{2+}(aq)}$

When $[\mathrm{Ni^{2+}}]$ = 0.20 M and $[\mathrm{Co^{2+}}]$ = 0.010 M,

a) What is the cell potential at these concentrations? In which direction does the reaction proceed spontaneously?

b) What are the concentrations of the metal ions when the battery is dead?

Standard reduction potentials:

$\mathrm{Co^{2+}(aq) + 2\,e^- \rightleftharpoons Co(s)} \quad E^\circ_{red} = -0.280\ V$

$\mathrm{Ni^{2+}(aq) + 2\,e^- \rightleftharpoons Ni(s)} \quad E^\circ_{red} = -0.260\ V$

Answer available at the end of this section.

Corrosion

Exercise 11.E.24*

Which member of each pair of metals is more likely to corrode (oxidize)?

a) Mg or Ca b) Au or Pb c) Fe or Zn d) Ag or Pt

Use the table of standard reduction potentials:

Metal	Reduction Half-Reaction	E°_{red} (V)
Gold (Au)	$\mathrm{Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s)}$	+1.50

Metal	Reduction Half-Reaction	E°_{red} (V)
Platinum (Pt)	$Pt^{2+}(aq) + 2\,e^- \longrightarrow Pt(s)$	+1.20
Silver (Ag)	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Lead (Pb)	$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	-0.13
Iron (Fe)	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	-0.45
Zinc (Zn)	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	-0.76
Magnesium (Mg)	$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	-2.37
Calcium (Ca)	$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	-2.87

Answer available at the end of this section.

Exercise 11.E.25**

Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank?
Note: Steel is an alloy composed mostly of iron.

Metal	Reduction Half-Reaction	E°_{red} (V)
Gold (Au)	$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s)$	+1.50
Silver (Ag)	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Nickel (Ni)	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$	-0.26
Iron (Fe)	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	-0.45
Zinc (Zn)	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	-0.76
Magnesium (Mg)	$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	-2.37

Answer available at the end of this section.

Electrolysis

Exercise 11.E.26**

Aluminum metal is produced industrially by the electrolysis of molten $AlCl_3(l)$. Write the half-reactions at the anode and cathode, calculate the standard cell potential, and explain why an external voltage is required for this process to occur.

Given standard reduction potentials:

- $Al^{3+}(l) + 3\,e^- \longrightarrow Al(l) \quad E^\circ_{red} = -1.66\ V$
- $Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(l) \quad E^\circ_{red} = +1.36\ V$

Answer available at the end of this section.

Exercise 11.E.27**

In the industrial electrolysis of molten $AlCl_3$, a current of 25.0 A is passed through the electrolytic cell for 4.00 hours.

a) How many grams of aluminum metal are produced?

b) What volume of chlorine gas (at STP) is produced at the anode?

Given:

- Molar mass of Al = 26.98 g/mol
- Faraday's constant = 96485 C/mol e^-
- Molar volume at STP = 22.4 L/mol

Answer available at the end of this section.

Exercise $11.E.28$**

A 12-V lead-acid car battery consists of 6 cells in series, each with the discharge reaction:

$$\mathrm{Pb\,(s) + PbO_2\,(s) + 2\,H_2SO_4\,(aq) \longrightarrow 2\,PbSO_4\,(s) + 2\,H_2O\,(l)}$$

When recharging, the battery is electrolyzed in the reverse direction. The relevant half-reactions during charging are:

At the cathode: $\mathrm{Pb^{2+}\,(aq) + 2\,e^- \longrightarrow Pb\,(s)}$

At the anode: $\mathrm{PbSO_4\,(s) + 2\,H_2O\,(l) \longrightarrow PbO_2\,(s) + 4\,H^+\,(aq) + SO_4{}^{2-}\,(aq) + 2\,e^-}$

If a current of 4.50 A is used to charge the battery for 8.00 hours, what mass of lead (Pb) is re-plated onto the cathode during recharging?

(Molar mass of Pb = 207.2 g/mol)

Answer available at the end of this section.

Additional Problems

Exercise $11.E.29$***

You have a galvanic cell at 25°C constructed as follows:

$$\mathrm{Pt\,(s)\ |\ H_2\,(g, 1\,atm)\ |\ H^+\,(aq, ?\,M)\ ||\ Ag^+(aq, 1.0\,M)|\ Ag\,(s)}$$

The measured cell potential is $E_{\mathrm{cell}} = 1.01\ \mathrm{V}$.

Given:

$\mathrm{2\,H^+\,(aq) + 2\,e^- \longrightarrow H_2\,(g)} \quad E^\circ_{\mathrm{red}} = 0.00\ \mathrm{V}$
$\mathrm{Ag^+\,(aq) + e^- \longrightarrow Ag\,(s)} \quad E^\circ_{\mathrm{red}}(\mathrm{Ag^+\ /\ Ag}) = +0.80\ \mathrm{V}$

Calculate the pH of the unknown acid solution.

Answer available at the end of this section.

Exercise $11.E.30$***

What is the minimum concentration of $\mathrm{Ag^+}$ required for the reaction to be spontaneous in the forward direction when [$\mathrm{Cu^{2+}}$]=1.00 M?

$$\mathrm{Cu(s) + 2\,Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2\,Ag(s)}$$

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad E^\circ_{\mathrm{red}} = +0.80\,\mathrm{V}$$

$$\mathrm{Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)} \qquad E^\circ_{\mathrm{red}} = +0.34\,\mathrm{V}$$

Answer available at the end of this section.

Exercise $11.E.31$***

Consider the galvanic cell at 25°C:

$$\mathrm{Fe(s) \mid Fe^{2+}\ (0.10\ M) \,||Cd^{2+}\ (1.00\ M) \mid Cd(s)}$$

Reduction half-reactions:

- $\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)} \quad E^\circ_{\mathrm{red}} = -0.45\ \mathrm{V}$
- $\mathrm{Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)} \quad E^\circ_{\mathrm{red}} = -0.40\ \mathrm{V}$

a) Calculate the standard cell potential, E°_{cell}.

b) Calculate the cell potential, E_{cell}, under the given non-standard conditions.

c) Calculate the equilibrium constant K for the cell reaction.

d) Calculate the equilibrium concentrations of $\mathrm{Fe^{2+}}$ and $\mathrm{Cd^{2+}}$.

e) Determine the mass of cadmium deposited on the electrode, assuming a volume of 1.00 L, as the cell reaches equilibrium.

f) If a current of $0.50\ \mathrm{A}$ is drawn from the cell, estimate how long it will take for equilibrium to be reached.

Answer available at the end of this section.

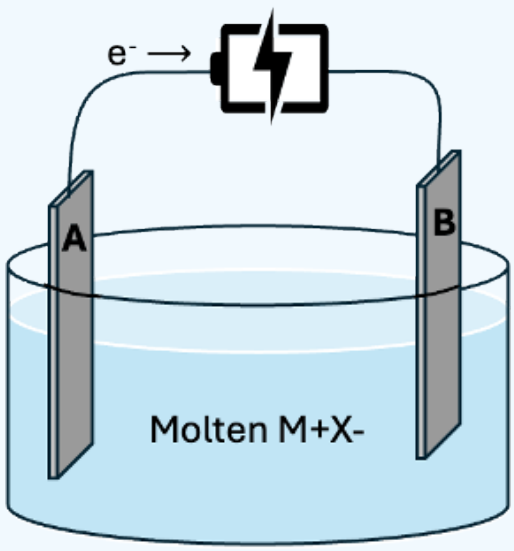
Exercise $11.E.32$**

If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.

Answer available at the end of this section.

Exercise $11.E.33$**

Consider the following electrolytic cell:



a) Label each electrode (A and B) as the anode and cathode.

b) Write the half-reaction that occurs at the cathode.

Answer available at the end of this section.

Answers

Exercise $11.E.1$*****

Oxidation is the loss of electrons, which increases the oxidation number of an element.
Reduction is the gain of electrons, which decreases the oxidation number of an element.

Oxidation and reduction always occur together in a chemical reaction because when one substance loses electrons (oxidation), another substance must gain those electrons (reduction). This is why these reactions are called redox (reduction-oxidation) reactions.

Exercise $11.E.2$*****

a) $\mathrm{Fe^{2+}}$ (oxidation number of Fe: +2) → $\mathrm{Fe^{3+}}$ (oxidation number of Fe: +3). The oxidation number increases, indicating a loss of electrons, which is oxidation.
$\mathrm{MnO_4^-}$ (oxidation number of Mn: +7) → $\mathrm{Mn^{2+}}$ (oxidation number of Mn: +2). The oxidation number decreases, indicating a gain of electrons, which is reduction.

b) Oxidizing agent: $\mathrm{MnO_4^-}$, because it causes $\mathrm{Fe^{2+}}$ to lose electrons while it is reduced itself.

Reducing agent: $\mathrm{Fe^{2+}}$, because it donates the electrons to reduce $\mathrm{MnO_4^-}$.

c) Write the oxidation and reduction half-reactions:

Oxidation: $\mathrm{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-}$

Reduction: $\mathrm{MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$

Exercise $11.E.3$*****

a) Zn (oxidation number of Zn: 0) → $\mathrm{Zn(OH)_4^{2-}}$ (oxidation number of Zn: +2). The oxidation number increases, indicating a loss of electrons, which is oxidation.
$\mathrm{Br_2}$ (oxidation number of Br: 0) → $\mathrm{Br^-}$ (oxidation number of Br: -1). The oxidation number decreases, indicating a gain of electrons, which is reduction.

b) Oxidizing agent: $\mathrm{Br_2}$, because it causes Zn to lose electrons while it is reduced itself.

Reducing agent: Zn, because it donates the electrons to reduce $\mathrm{Br_2}$.

c) Oxidation: $\mathrm{Zn(s) + 4\,OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2\,e^-}$

Reduction: $\mathrm{Br_2(l) + 2\,e^- \rightarrow 2\,Br^-(aq)}$

Exercise $11.E.4$******

a) Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$
$$\text{reduction:} \quad \mathrm{NO_3^-(aq) \longrightarrow NO(g)}$$

Step 2: Balance each half-reaction for all elements except H and O. **Complete!**

Step 3: Balance each half-reaction for $\mathbf{O}$ by adding $\mathbf{H2O}$:

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$
$$\text{reduction:} \quad \mathrm{NO_3^-(aq) \longrightarrow NO(g) + \mathbf{2H2O(l)}}$$

Step 4: Balance each half-reaction for $\mathbf{H}$ by adding $\mathbf{H^+}$:

$$\text{oxidation:} \quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)}$$
$$\text{reduction:} \quad \mathbf{4H^{+}(aq)} + \mathrm{NO_3{}^{-}\,(aq) \longrightarrow NO\,(g) + 2\,H_2O\,(l)}$$

Step 5: Balance each half-reaction for **charge** by adding **electrons:**

$$\text{oxidation:} \quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)} + \mathbf{2e^{-}}$$
$$\text{reduction:} \quad \mathbf{3e^{-}} + \mathrm{4\,H^{+}\,(aq) + NO_3{}^{-}\,(aq) \longrightarrow NO\,(g) + 2\,H_2O\,(l)}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons gained equals the number lost:

$$\text{oxidation: } (\times 3) \quad \mathbf{3}\mathrm{Cu\,(s) \longrightarrow 3Cu^{2+}\,(aq)} + \mathbf{6}\ \mathrm{e^{-}}$$
$$\text{reduction: } (\times 2) \quad \mathbf{6}\ \mathrm{e^{-}} + \mathbf{8}\ \mathrm{H^{+}\,(aq)} + \mathbf{2}\mathrm{NO_3{}^{-}\,(aq) \longrightarrow 2\ NO\,(g) + 4\ H_2O\,(l)}$$

Step 7: Add the two half-reactions and simplify:

$$\mathrm{3\,Cu\,(s)} + \cancel{\mathrm{6e^{-}}} + \mathrm{8\,H^{+}\,(aq) + 2\,NO_3{}^{-}\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq)} + \cancel{\mathrm{6e^{-}}} + \mathrm{2\,NO\,(g) + 4\,H_2O\,(l)}$$
$$\mathrm{3\,Cu\,(s) + 8\,H^{+}\,(aq) + 2\,NO_3{}^{-}\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)}$$

Final Check

Element	Reactants	Products
Cu	3	3
H	8	8
N	2	2
O	6	6

Reactants: $3 \times 0\ (\mathrm{Cu}) + 8 \times (+1)\ (\mathrm{H^{+}}) + 2 \times (-1)\ (\mathrm{NO_3{}^{-}}) = +6$ Products: $3 \times (+2)\ (\mathrm{Cu^{2+}}) + 2 \times 0\,(\mathrm{NO}) + 4 \times 0\,(\mathrm{H_2O}) = +6$
Both atoms and total charge are balanced.

b) Step 1: Write skeletal equations for the oxidation and reduction half-reactions:

$$\text{oxidation:} \quad \mathrm{Ni\,(s) \longrightarrow Ni^{2+}\,(aq)}$$
$$\text{reduction:} \quad \mathrm{Cr_2O_7{}^{2-}\,(aq) \longrightarrow Cr^{3+}\,(aq)}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad \mathrm{Ni\,(s) \longrightarrow Ni^{2+}\,(aq)}$$
$$\text{reduction:} \quad \mathrm{Cr_2O_7{}^{2-}\,(aq) \longrightarrow 2Cr^{3+}\,(aq)}$$

Step 3: Balance each half-reaction for O by adding H2O:

$$\text{oxidation:} \quad \mathrm{Ni\,(s) \longrightarrow Ni^{2+}\,(aq)}$$
$$\text{reduction:} \quad \mathrm{Cr_2O_7{}^{2-}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq)} + \mathbf{7H2O(l)}$$

Step 4: Balance each half-reaction for H by adding $\mathrm{H^{+}}$:

$$\text{oxidation:} \quad \mathrm{Ni\,(s) \longrightarrow Ni^{2+}\,(aq)}$$
$$\text{reduction:} \quad \mathbf{14H^{+}(aq)} + \mathrm{Cr_2O_7{}^{2-}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)}$$

Step 5: Balance each half-reaction for **charge** by adding **electrons:**

$$\text{oxidation:} \quad \mathrm{Ni\,(s) \longrightarrow Ni^{2+}\,(aq)} + \mathbf{2e^{-}}$$
$$\text{reduction:} \quad \mathbf{6e^{-}} + \mathrm{14\,H^{+}\,(aq) + Cr_2O_7{}^{2-}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons gained equals the number lost:

$$\text{oxidation: } (\times 3) \quad \mathbf{3}\mathrm{Ni\,(s) \longrightarrow 3Ni^{2+}\,(aq)} + \mathbf{6}\ \mathrm{e^{-}}$$
$$\text{reduction:} \quad \mathrm{6\,e^{-} + 14\,H^{+}\,(aq) + Cr_2O_7{}^{2-}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)}$$

Step 7: Add the two half-reactions and simplify:

$$\mathrm{3\,Ni\,(s)} + \cancel{\mathrm{6e^{-}}} + \mathrm{14\,H^{+}\,(aq) + Cr_2O_7{}^{2-}\,(aq) \longrightarrow 3\,Ni^{2+}\,(aq)} + \cancel{\mathrm{6e^{-}}} + \mathrm{2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)}$$
$$\mathrm{3\,Ni\,(s) + 14\,H^{+}\,(aq) + Cr_2O_7{}^{2-}\,(aq) \longrightarrow 3\,Ni^{2+}\,(aq) + 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)}$$

Final Check

Element	Reactants	Products
Ni	3	3
H	14	14
Cr	2	2
O	7	7

Charge

Reactants: +12, Products +12

Both atoms and total charge are balanced.

c) Step 1: Write skeletal equations for the oxidation and reduction half-reactions:

$$\text{oxidation:} \quad C_2O_4{}^{2-}(aq) \longrightarrow CO_2(g)$$

$$\text{reduction:} \quad MnO_4{}^{-}(aq) \longrightarrow Mn^{2+}(aq)$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad C_2O_4{}^{2-}(aq) \longrightarrow \mathbf{2}CO_2(g)$$

$$\text{reduction:} \quad MnO_4{}^{-}(aq) \longrightarrow Mn^{2+}(aq)$$

Step 3: Balance each half-reaction for O by adding H2O:

$$\text{oxidation:} \quad C_2O_4{}^{2-}(aq) \longrightarrow 2\,CO_2(g)$$

$$\text{reduction:} \quad MnO_4{}^{-}(aq) \longrightarrow Mn^{2+}(aq) + \mathbf{4H2O(l)}$$

Step 4: Balance each half-reaction for H by adding H^+:

$$\text{oxidation:} \quad C_2O_4{}^{2-}(aq) \longrightarrow 2\,CO_2(g)$$

$$\text{reduction:} \quad \mathbf{8H^+(aq)} + MnO_4{}^{-}(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Step 5: Balance each half-reaction for **charge** by adding **electrons:**

$$\text{oxidation:} \quad C_2O_4{}^{2-}(aq) \longrightarrow 2\,CO_2(g) + \mathbf{2e^-}$$

$$\text{reduction:} \quad \mathbf{5e^-} + 8\,H^+(aq) + MnO_4{}^{-}(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons gained equals the number lost:

$$\text{oxidation: } (\times 5) \quad \mathbf{5}C_2O_4{}^{2-}(aq) \longrightarrow \mathbf{10}CO_2(g) + \mathbf{10}e^-$$

$$\text{reduction: } (\times 2) \quad \mathbf{10}e^- + \mathbf{16}H^+(aq) + \mathbf{2}MnO_4{}^{-}(aq) \longrightarrow \mathbf{2}Mn^{2+}(aq) + \mathbf{8}H_2O(l)$$

Step 7: Add the two half-reactions and simplify:

$$5\,C_2O_4{}^{2-}(aq) + \cancel{10e^-} + 16\,H^+(aq) + 2\,MnO_4{}^{-}(aq) \longrightarrow 10\,CO_2(g) + \cancel{10e^-} + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$

$$5\,C_2O_4{}^{2-}(aq) + 16\,H^+(aq) + 2\,MnO_4{}^{-}(aq) \longrightarrow 10\,CO_2(g) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$

Final Check

Element	Reactants	Products
C	10	10
O	28	28
H	16	16
Mn	2	2

Charge: Reactants +4, Products +4

Both atoms and total charge are balanced.

Exercise $11.E.5$***

a) Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad IO_3{}^{-}(aq) \longrightarrow IO_4{}^{-}(aq)$$

$$\text{reduction:} \quad MnO_4{}^{-}(aq) \longrightarrow MnO_2(s)$$

Step 2: Balance each half-reaction for all elements except H and O. **Complete!**

Step 3: Balance each half-reaction for O by adding H2O.

$$\text{oxidation:} \quad \mathbf{H2O(l)} + IO_3{}^{-}(aq) \longrightarrow IO_4{}^{-}(aq)$$

$$\text{reduction:} \quad MnO_4{}^{-}(aq) \longrightarrow MnO_2(s) + \mathbf{2H2O(l)}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\text{oxidation:} \quad H_2O(l) + IO_3{}^{-}(aq) \longrightarrow IO_4{}^{-}(aq) + \mathbf{2H + (aq)}$$

$$\text{reduction:} \quad \mathbf{4H + (aq)} + MnO_4{}^{-}(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad H_2O(l) + IO_3{}^{-}(aq) \longrightarrow IO_4{}^{-}(aq) + 2\,H^+(aq) + \mathbf{2e-}$$

$$\text{reduction:} \quad \mathbf{3e-} + 4\,H^+(aq) + MnO_4{}^{-}(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Step 6: If necessary, multiply one or both half-reactions; so that the number of electrons gained equals the number lost.

$$\text{oxidation: } (\times 3) \quad \mathbf{3}H_2O(l) + \mathbf{3}IO_3{}^{-}(aq) \longrightarrow \mathbf{3}IO_4{}^{-}(aq) + \mathbf{6}H^+(aq) + \mathbf{6}e^-$$

$$\text{reduction: } (\times 2) \quad \mathbf{6}e^- + \mathbf{8}H^+(aq) + \mathbf{2}MnO_4{}^{-}(aq) \longrightarrow \mathbf{2}MnO_2(s) + \mathbf{4}H_2O(l)$$

Step 7: Add the two half-reactions and simplify.

$$\cancel{3H2O(l)} + 3\,IO_3^-(aq) + \cancel{6e^-} + 2\,\cancel{8}\,H^+(aq) + 2\,MnO_4^-(aq) \longrightarrow 3\,IO_4^-(aq) + \cancel{6H^+}(aq) + \cancel{6e^-} + 2\,MnO_2(s) + 1\,\cancel{4}\,H_2O(l)$$

$$3\,IO_3^-(aq) + 2\,H^+(aq) + 2\,MnO_4^-(aq) \longrightarrow 3\,IO_4^-(aq) + 2\,MnO_2(s) + H_2O(l)$$

Step 8: If the reaction takes place in basic solution, add OH^- ions to both sides to neutralize the H^+ ions, then simplify (remembering that $H^+ + OH^- \rightarrow H_2O(l)$):

$$3\,IO_3^-(aq) + \mathbf{2H} + \mathbf{(aq)} + \mathbf{2OH} - \mathbf{(aq)} + 2\,MnO_4^-(aq) \longrightarrow 3\,IO_4^-(aq) + 2\,MnO_2(s) + H_2O(l) + \mathbf{2OH^-(aq)}$$

$$3\,IO_3^-(aq) + \mathbf{2H2O(l)} + 2\,MnO_4^-(aq) \longrightarrow 3\,IO_4^-(aq) + 2\,MnO_2(s) + H_2O(l) + \mathbf{2OH^-(aq)}$$

$$3\,IO_3^-(aq) + \cancel{2}\,H_2O(l) + 2\,MnO_4^-(aq) \longrightarrow 3\,IO_4^-(aq) + 2\,MnO_2(s) + \cancel{H2O(l)} + 2\,OH^-(aq)$$

$$3\,IO_3^-(aq) + H_2O(l) + 2\,MnO_4^-(aq) \longrightarrow 3\,IO_4^-(aq) + 2\,MnO_2(s) + 2\,OH^-(aq)$$

Final Check

Element	Reactants	Products
I	3	3
O	18	18
H	2	2
Mn	2	2

Total Charge:

Reactants: -3 + 0 + -2 = -5 Products: -3 + 0 + -2 = -5

Both atoms and total charge are balanced.

b) Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad Cr(OH)_4^-(aq) \longrightarrow CrO_4^{2-}(aq)$$

$$\text{reduction:} \quad ClO^-(aq) \longrightarrow Cl_2(g)$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad Cr(OH)_4^-(aq) \longrightarrow CrO_4^{2-}(aq)$$

$$\text{reduction:} \quad \mathbf{2}ClO^-(aq) \longrightarrow Cl_2(g)$$

Step 3: Balance each half-reaction for O by adding $\mathbf{H2O}$.

$$\text{oxidation:} \quad Cr(OH)_4^-(aq) \longrightarrow CrO_4^{2-}(aq)$$

$$\text{reduction:} \quad 2\,ClO^-(aq) \longrightarrow Cl_2(g) + \mathbf{2H2O(l)}$$

Step 4: Balance each half-reaction for H by adding $\mathbf{H^+}$.

$$\text{oxidation:} \quad Cr(OH)_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + \mathbf{4}H^+$$

$$\text{reduction:} \quad \mathbf{4}H^+ + 2\,ClO^-(aq) \longrightarrow Cl_2(g) + 2\,H_2O(l)$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad Cr(OH)_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + 4\,H^+ + \mathbf{3}e-$$

$$\text{reduction:} \quad \mathbf{2}e- + 4\,H^+ + 2\,ClO^-(aq) \longrightarrow Cl_2(g) + 2\,H_2O(l)$$

Step 6: If necessary, multiply one or both half-reactions; so that the number of electrons gained equals the number lost.

$$\text{oxidation:(x2):} \quad \mathbf{2}Cr(OH)_4^-(aq) \longrightarrow \mathbf{2}CrO_4^{2-}(aq) + \mathbf{8}H^+ + \mathbf{6}e^-$$

$$\text{reduction(x3):} \quad \mathbf{6}e^- + \mathbf{12}H^+ + \mathbf{6}ClO^-(aq) \longrightarrow \mathbf{3}Cl_2(g) + \mathbf{6}H_2O(l)$$

Step 7: Add the two half-reactions and simplify.

$$2\,Cr(OH)_4^-(aq) + \cancel{6e^-} + \cancel{4\,12}\,H^+ + 6\,ClO^-(aq) \longrightarrow 2\,CrO_4^{2-}(aq) + \cancel{8H^+} + \cancel{6e^-} + 3\,Cl_2(g) + 6\,H_2O(l)$$

$$2\,Cr(OH)_4^-(aq) + 4\,H^+ + 6\,ClO^-(aq) \longrightarrow 2\,CrO_4^{2-}(aq) + 3\,Cl_2(g) + 6\,H_2O(l)$$

Step 8: If the reaction takes place in basic solution, add OH^- ions to both sides to neutralize the H^+ ions, then simplify (remembering that $H^+ + OH^- \rightarrow H_2O(l)$):

$$2\,Cr(OH)_4^-(aq) + 4\,H^+ + \mathbf{4OH}- + 6\,ClO^-(aq) \longrightarrow 2\,CrO_4^{2-}(aq) + 3\,Cl_2(g) + 6\,H_2O(l) + \mathbf{4OH}-$$

$$2\,Cr(OH)_4^-(aq) + \cancel{\mathbf{4H2O}} + 6\,ClO^-(aq) \longrightarrow 2\,CrO_4^{2-}(aq) + 3\,Cl_2(g) + \mathbf{2}\,\cancel{6}\,H_2O(l) + 4\,OH^-$$

$$2\,Cr(OH)_4^-(aq) + 6\,ClO^-(aq) \longrightarrow 2\,CrO_4^{2-}(aq) + 3\,Cl_2(g) + 2\,H_2O(l) + 4\,OH^-$$

Final Check

Element	Reactants	Products
Cr	2	2
O	14	14
H	8	8
Cl	6	6

Total Charge:

Reactants: -2 + -6 = -8 Products: -4 + 0 + 0 + -4 = -8

Both atoms and total charge are balanced.

Exercise $11.E.6$*****

a) The anode is the electrode where oxidation occurs and the electrons leave the electrode: **A**.

b) The cathode is the electrode where reduction occurs (gaining electrons): **E**.

c) The salt bridge is the U-shaped tube that allows ion flow to maintain charge balance between the half-cells: **C**.

d) The anode has a negative charge because it is the source of electrons in the external circuit: **A**.

Exercise $11.E.7$******

a) Since electrons are leaving the Pb electrode, it is the anode where oxidation occurs.

b) Cu gains the electrons, so it is the cathode.

c) The cathode (Cu electrode) has a positive charge.

d) Anode (oxidation): $\mathrm{Pb(s)} \rightarrow \mathrm{Pb^{2+}(aq)} + 2\,\mathrm{e^-}$

Cathode (reduction): $\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Cu(s)}$

Overall: $\mathrm{Pb(s)} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Pb^{2+}(aq)} + \mathrm{Cu(s)}$

e) As the cell operates, the lead electrode is oxidized and loses mass into solution, $\mathrm{Pb(s)} \rightarrow \mathrm{Pb^{2+}(aq)} + 2\,\mathrm{e^-}$.

f) The copper electrode could be replaced with Pt, since Cu is not oxidized in this galvanic cell.

g) $\mathrm{Pb(s)} \mid \mathrm{Pb^{2+}(aq)} \,||\, \mathrm{Cu^{2+}(aq)} \mid \mathrm{Cu(s)}$

Exercise $11.E.8$******

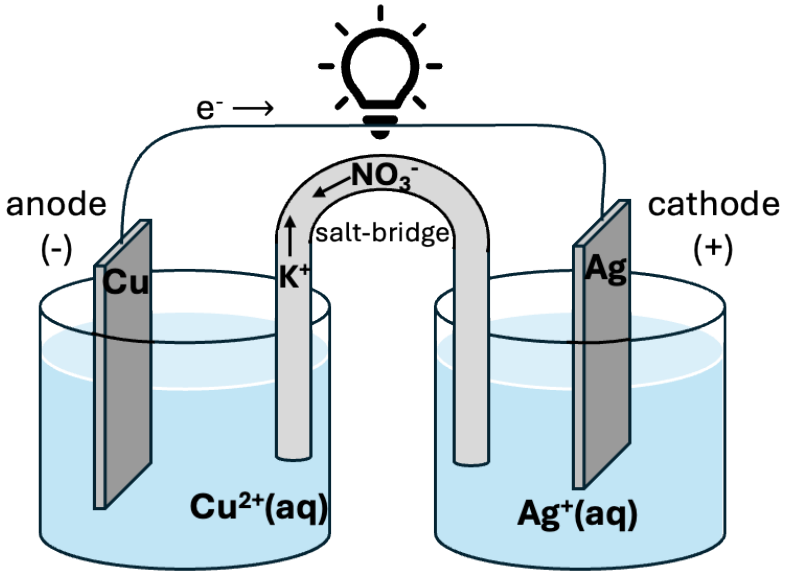
a) Since the copper electrode is negative, it is the anode where oxidation occurs:

Anode (oxidation): $\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-}$

Cathode (reduction): $\mathrm{Ag^{+}(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}$

Overall: $\mathrm{Cu(s)} + 2\,\mathrm{Ag^{+}(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{Ag(s)}$

b)



Exercise $11.E.9$******

The shorthand notation lists the anode on the left and the cathode on the right, with electrodes on the outside. Phases are separated by a single vertical line (|), and the two half-cells are separated by a double line (||).

If all species are in solution in a half-cell, a platinum electrode is used.

a) $\mathrm{Mg(s)} \mid \mathrm{Mg^{2+}\,(aq)} \parallel \mathrm{Ni^{2+}\,(aq)} \mid \mathrm{Ni(s)}$

b) $\mathrm{Cu(s)} \mid \mathrm{Cu^{2+}(aq)} \parallel \mathrm{Ag^{+}\,(aq)} \mid \mathrm{Ag(s)}$

c) $\mathrm{Mn(s)} \mid \mathrm{Mn^{2+}(aq)} \parallel \mathrm{Sn^{2+}\,(aq)} \mid \mathrm{Sn(s)}$

d) Since both $\mathrm{Cu^{+}}$ and $\mathrm{Cu^{2+}}$ are in solution in the anode compartment, a platinum electrode is required:

$\mathrm{Pt(s)} \mid \mathrm{Cu^{+}(aq)},\ \mathrm{Cu^{2+}(aq)} \parallel \mathrm{Au^{3+}\,(aq)} \mid \mathrm{Au(s)}$

Exercise $11.E.10$*****

Without a salt bridge, the circuit would be incomplete, and no current could flow between the two half-cells. As the redox reaction proceeds, charge buildup would occur in each half-cell (excess positive in the oxidation half-cell, excess negative in the reduction half-cell), stopping the flow of electrons through the external circuit.

The salt bridge allows ions to flow between the half-cells to maintain electrical neutrality, completing the circuit and allowing electrons to continue flowing through the wire so the redox reaction (and current) can continue.

Exercise $11.E.11$*****

The standard cell potential (E°_{cell}) indicates the driving force for the redox reaction under standard conditions (1 M concentrations, 1 atm pressure, 25°C):

If E°_{cell} > 0, the redox reaction is spontaneous as written, and the galvanic cell can produce electrical energy. If E°_{cell} < 0, the redox reaction is non-spontaneous as written, and the reverse reaction would be spontaneous.

The larger the positive value of E°_{cell}, the greater the tendency for the redox reaction to occur spontaneously, meaning the cell can produce a higher voltage.

In essence, E°_{cell} helps us predict whether a redox reaction will proceed spontaneously and how much electrical energy can be harnessed from it under standard conditions.

Exercise $11.E.12$*****

Step 1: Identify which half-reaction occurs at the cathode (reduction) and which at the anode (oxidation).

Step 2: Balance electrons if needed and write the balanced overall reaction.

Step 3: Use $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$ to calculate the standard cell potential.

a) reduction (cathode):$\mathrm{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)} \quad E^\circ_{red} = 0.77\ \mathrm{V}$

oxidation (anode):$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-} \quad E^\circ_{ox} = -E^\circ_{red} = +0.76\ \mathrm{V}$

To balance the electrons, the reduction reaction must be multiplied by two.

Overall: $\mathrm{2\,Fe^{3+}(aq) + Zn(s) \rightarrow 2\,Fe^{2+}(aq) + Zn^{2+}(aq)}$

$E^\circ_{cell} = 0.77\ \mathrm{V} + 0.76\ \mathrm{V} = 1.53\ \mathrm{V}$

The large, positive (E°_{cell}) indicates the reaction is spontaneous under standard conditions, and the cell would function well as a galvanic cell.

b) reduction (cathode):$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)} \quad E^\circ_{red} = 0.34\ \mathrm{V}$

oxidation (anode):$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-} \quad E^\circ_{ox} = -E^\circ_{red} = +0.76\ \mathrm{V}$

Overall: $\mathrm{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$

$E^\circ_{cell} = 0.34\ \mathrm{V} + 0.76\ \mathrm{V} = 1.10\ \mathrm{V}$

The positive (E°_{cell}) indicates the reaction is spontaneous under standard conditions, and the cell would function well as a galvanic cell.

c) reduction (cathode):$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)} \quad E^\circ_{red} = 0.34\ \mathrm{V}$

oxidation (anode):$\mathrm{Cd(s) \rightarrow Cd^{2+}(aq) + 2\,e^-} \quad E^\circ_{ox} = -E^\circ_{red} = +0.40\ \mathrm{V}$

Overall: $\mathrm{Cu^{2+}(aq) + Cd(s) \rightarrow Cu(s) + Cd^{2+}(aq)}$

$E^\circ_{cell} = 0.34\ \mathrm{V} + 0.40\ \mathrm{V} = 0.74\ \mathrm{V}$

The positive (E°_{cell}) indicates the reaction is spontaneous under standard conditions, and the cell would function well as a galvanic cell.

d) reduction (cathode): $\mathrm{Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)} E^\circ_{red} = 1.36\ \mathrm{V}$

oxidation (anode): $\mathrm{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-(aq)} \quad E^\circ_{ox} = -E^\circ_{red} = -0.77\ \mathrm{V}$

To balance the electrons, the oxidation reaction must be multiplied by two.

Overall: $\mathrm{2\,Fe^{2+}(aq) + Cl_2(g) \rightarrow 2\,Fe^{3+}(aq) + 2\,Cl^-(aq)}$

$E^\circ_{cell} = 1.36\ \mathrm{V} + -0.77\ \mathrm{V} = 0.59\ \mathrm{V}$

The positive (E°_{cell}) indicates the reaction is spontaneous under standard conditions, and the cell would function well as a galvanic cell.

Exercise $11.E.13$******

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad \mathrm{Mn^{2+}(aq) \longrightarrow MnO_4^-(aq)}$$
$$\text{reduction:} \quad \mathrm{Cl_2(g) \rightarrow 2\,Cl^-(aq)}$$

Step 2: Balance each half-reaction for all elements except H and O. Complete!

Step 3: Balance each half-reaction for **O** by adding **H2O**:

$$\text{oxidation:} \quad \mathrm{4\,H_2O(l) + Mn^{2+}(aq) \longrightarrow MnO_4^-(aq)}$$
$$\text{reduction:} \quad \mathrm{Cl_2(g) \rightarrow 2\,Cl^-(aq)}$$

Step 4: Balance each half-reaction for **H** by adding $\mathbf{H^+}$:

$$\text{oxidation:} \quad \mathrm{4\,H_2O(l) + Mn^{2+}(aq) \longrightarrow MnO_4^-(aq) + 8\,H^+(aq)}$$
$$\text{reduction:} \quad \mathrm{Cl_2(g) \rightarrow 2\,Cl^-(aq)}$$

Step 5: Balance each half-reaction for charge by adding electrons:

$$\text{oxidation:} \quad \mathrm{4\,H_2O(l) + Mn^{2+}(aq) \longrightarrow MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-}$$
$$\text{reduction:} \quad \mathrm{Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons gained equals the number lost:

$$\text{oxidation: } (\times 2) \quad \mathrm{8\,H_2O(l) + 2\,Mn^{2+}(aq) \longrightarrow 2\,MnO_4^-(aq) + 16\,H^+(aq) + 10\,e^-}$$
$$\text{reduction: } (\times 5) \quad \mathrm{5\,Cl_2(g) + 10\,e^- \rightarrow 10\,Cl^-(aq)}$$

Step 7: Add the two half-reactions and simplify:

$$\mathrm{8\,H_2O(l) + 2\,Mn^{2+}(aq) + 5\,Cl_2(g) + \cancel{10e^-} \longrightarrow 2\,MnO_4^-(aq) + 16\,H^+(aq) + \cancel{10e^-} + 10\,Cl^-(aq)}$$
$$\mathrm{8\,H_2O(l) + 2\,Mn^{2+}(aq) + 5\,Cl_2(g) \longrightarrow 2\,MnO_4^-(aq) + 16\,H^+(aq) + 10\,Cl^-(aq)}$$

A good final check is to verify that both atom counts and total charge are balanced:

H: 16 ✓, O: 8 ✓, Mn: 2 ✓, Cl: 10 ✓ Charges: 4+ each side ✓

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = -1.51\ \mathrm{V} + 1.36\ \mathrm{V} = -0.15\ \mathrm{V}$

Since the standard cell potential is negative, the redox reaction is nonspontaneous under standard state conditions.

Exercise $11.E.14$******

Strongest oxidizing agent:

The species with the highest (most positive) E°_{red} will most readily gain electrons: $\mathrm{Ag^+}$.

Strongest reducing agent: The reducing agent is being oxidized, so we need to consider the oxidation reactions, the reverse of the reduction reactions. The species with the lowest (most negative) E°_{red} will most readily lose electrons (as its oxidation potential is highest): $\mathrm{Ca(s)}$.

Exercise $11.E.15$***

a) Strongest oxidizing agent:
The species with the highest (most positive) E°_{red} will most readily gain electrons: $\mathrm{S_2O_8{}^{2-}(aq)}$.

Strongest reducing agent: The reducing agent is being oxidized, so we need to consider the oxidation reactions, the reverse of the reduction reactions. The species with the lowest (most negative) E°_{red} will most readily lose electrons (as its oxidation potential is highest): $\mathrm{Fe(s)}$.

b) To write redox reactions, we need one reduction half-reaction and one oxidation half-reaction. To give a spontaneous reaction, we need a positive value of (E°_{cell}).

Reaction 1:

To get the highest possible (E°_{cell}), we would take the largest reduction potential and the smallest (most negative) reduction potential, which we will reverse to give the oxidation half reaction:

reduction: $\mathrm{S_2O_8{}^{2-}(aq) + 2\,e^- \longrightarrow 2\,SO_4{}^{2-}(aq)} \quad E^\circ_{red} = 2.01\ V$

oxidation: $\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-} \quad E^\circ_{ox} = -E^\circ_{red} = +0.45\ V$

overall: $\mathrm{S_2O_8{}^{2-}(aq) + Fe(s) \longrightarrow 2\,SO_4{}^{2-}(aq) + Fe^{2+}(aq)}$

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 0.45\ \mathrm{V} + 2.01\ \mathrm{V} = 2.46\ \mathrm{V}$

Reaction 2:

reduction: $\mathrm{S_2O_8{}^{2-}(aq) + 2\,e^- \longrightarrow 2\,SO_4{}^{2-}(aq)} \quad E^\circ_{red} = 2.01\ V$

oxidation: $\mathrm{Sn(s) \longrightarrow Sn^{2+}(aq) + 2\,e^-} \quad E^\circ_{ox} = -E^\circ_{red} = +0.14\ V$

overall: $\mathrm{S_2O_8{}^{2-}(aq) + Sn(s) \longrightarrow 2\,SO_4{}^{2-}(aq) + Sn^{2+}(aq)}$

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 0.14\ \mathrm{V} + 2.01\ \mathrm{V} = 2.15\ \mathrm{V}$

Reaction 3:

reduction: $\mathrm{Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)} \quad E^\circ_{red} = -0.14\ V$

oxidation: $\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-} \quad E^\circ_{ox} = -E^\circ_{red} = +0.45\ V$

overall: $\mathrm{Sn^{2+}(aq) + Fe(s) \longrightarrow Sn(s) + Fe^{2+}(aq)}$

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 0.45\ \mathrm{V} + -0.14\ \mathrm{V} = 0.31\ \mathrm{V}$

Exercise $11.E.16$*

a) Oxidation: $\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \quad E^\circ_{ox} = -0.34\ V$

Reduction: $\mathrm{Sn^{4+}(aq) + 2\,e^- \rightarrow Sn^{2+}(aq)} \quad E^\circ_{red} = 0.15\ V$

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = -0.34\ V + 0.15\ V = -0.19\ V$

Since E°_{cell} is negative, ΔG° must be positive:

$\Delta G^\circ = -nFE^\circ_{cell} = -2(96485\ C/mol)(-0.19\ J/C) = 36664\ J/mol = 37\ kJ/mol$

The reaction is non-spontaneous under standard state conditions.

b) Oxidation: $\mathrm{2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-} \quad E^\circ_{ox} = -1.23\ V$

Reduction: $\mathrm{2\,Cl_2(g) + 4\,e^- \rightarrow 4\,Cl^-(aq)} \quad E^\circ_{red} = 1.36\ V$

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = -1.23\ V + 1.36\ V = 0.13\ V$

Since E°_{cell} is positive, ΔG° must be negative:

$\Delta G^\circ = -nFE^\circ_{cell} = -4(96485\ C/mol)(0.13\ J/C) = -50172\ J/mol = -50\ kJ/mol$

The reaction is spontaneous under standard state conditions.

Exercise $11.E.17$*

a) Reaction: $\mathrm{Ca^{2+}(aq) + 2\,Li(s) \rightleftharpoons Ca(s) + 2\,Li^+(aq)}$

Half-reactions:

Reduction: $\mathrm{Ca^{2+}(aq) + 2\,e^- \rightleftharpoons Ca(s)} \quad E^\circ_{red} = -2.87\ V$

Oxidation: $\mathrm{2\,Li(s) \rightleftharpoons 2\,Li^+(aq) + 2\,e^-} \quad E^\circ_{ox} = 3.04\ V$

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 3.04\,V + (-2.87\,V) = 0.17\,V$$

Calculate K:

$$E^\circ_{cell} = \frac{RT}{nF}\ln K \quad \rightarrow \quad \ln K = \frac{nFE^\circ_{cell}}{RT}$$

Using $n = 2$, $F = 96485\ C/mol$, $R = 8.314\ J/(mol \cdot K)$, and $T = 298\ K$:

$$\ln K = \frac{(2)(96485)(0.17)}{8.314 \times 298} = 13.24$$

$$K = e^{13.24} = 5.6 \times 10^5$$

This large K indicates the reaction is strongly product-favoured.

b) Reaction: $\mathrm{Cu^{2+}(aq) + Ni(OH)_2(s) + 2\,OH^-(aq) \rightleftharpoons Cu(s) + NiO_2(s) + 2\,H_2O(l)}$

Half-reactions:

Reduction: $\mathrm{Cu^{2+}(aq) + 2\,e^- \rightleftharpoons Cu(s)} \quad E^\circ_{red} = 0.34\ V$

Oxidation: $\mathrm{Ni(OH)_2(s) + 2\,OH^-(aq) \rightleftharpoons NiO_2(s) + 2\,H_2O(l) + 2\,e^-} \quad E^\circ_{ox} = -0.49\ V$

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = -0.49\,V + 0.34\,V = -0.15\,V$$

Calculate K:

$$\ln K = \frac{(2)(96485)(-0.15)}{8.314 \times 298} = -11.68$$

$$K = e^{-11.68} = 8.5 \times 10^{-6}$$

This very small K indicates the reaction is strongly reactant-favoured.

Exercise $11.E.18$*

To find K, we need to know how many electrons are transferred in the reaction:

In $\mathrm{Br^-}$, the oxidation number of Br is -1. In $\mathrm{Br_2}$, the oxidation number is 0. Each Br loses 1 electron, so a total of 6 electrons are transferred in the redox reaction.

Similarly, in $\mathrm{Cr_2O_7^{2-}}$, the oxidation number of Cr is +6. In $\mathrm{Cr^{3+}}$, the oxidation number is +3. Each Cr gains 3 electrons, so a total of 6 electrons.

$$\begin{aligned} E^\circ_{cell} &= \frac{RT}{nF}\ln K \\ &= \frac{(8.314\,\mathrm{J\ mol^{-1}K^{-1}})(298\,\mathrm{K})}{(6)(96485\,\mathrm{C\ mol^{-1}})}\ln(2.32\times10^{27}) \\ &= 0.270\,\mathrm{V} \end{aligned}$$

$\Delta G^\circ = -nFE^\circ_{cell} = -6(96485\ \mathrm{C/mol})(0.270\ \mathrm{J/C}) = -1.56\times10^5\ \mathrm{J/mol} = -156\ \mathrm{kJ/mol}$

The reaction is spontaneous under standard state conditions. This is confirmed by the positive value of E°_{cell} and the negative value of ΔG°.

Exercise $11.E.19$**

a) $E^\circ_{cell} = 0.34\ \mathrm{V} + 0.76\ \mathrm{V} = 1.10\ \mathrm{V}$

b)

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]}$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]}$$

Since the concentration of the reactant ($\mathrm{Cu^{2+}}$) is higher and the concentration of the product ($\mathrm{Zn^{2+}}$) is lower than under standard conditions, the cell is further from equilibrium, so the cell potential should be greater than the standard cell potential.

$$E_{cell} = 1.10\ \mathrm{V} - \frac{(8.314\frac{\mathrm{J}}{\mathrm{mol\cdot K}})(298\ \mathrm{K})}{2(96485\,\mathrm{C/mol})}\ln\frac{(0.10)}{(1.5)} = 1.13\ \mathrm{V}$$

As predicted, the cell potential is greater than the standard cell potential.

c) Since the concentration of the reactant ($\mathrm{Cu^{2+}}$) is lower and the concentration of the product ($\mathrm{Zn^{2+}}$) is higher than under standard conditions, the cell potential should be lower than the standard cell potential.

$$E_{cell} = 1.10\ \mathrm{V} - \frac{(8.314\frac{\mathrm{J}}{\mathrm{mol\cdot K}})(298\ \mathrm{K})}{2(96485\,\mathrm{C/mol})}\ln\frac{(1.5)}{(0.50)} = 1.09\ \mathrm{V}$$

As predicted, the cell potential is lower than the standard cell potential.

Exercise $11.E.20$**

From the cell notation, $\mathrm{Zn\,(s)}$ is at the anode (left), meaning it is oxidized. $\mathrm{Ag^+}$ is at the cathode (right), so it is reduced.

This also agrees with standard reduction potentials: $\mathrm{Ag^+}$ has a higher reduction potential than $\mathrm{Zn^{2+}}$, so silver ions are reduced and zinc metal is oxidized.

Oxidation: $\mathrm{Zn\,(s)} \rightleftharpoons \mathrm{Zn^{2+}\,(aq) + 2\,e^-} \quad E^\circ_{ox} = +0.76\ V$

Reduction: $\mathrm{2\,Ag^+\,(aq) + 2\,e^-} \rightleftharpoons \mathrm{2\,Ag\,(s)} \quad E^\circ_{red} = 0.80\ V$

Net Reaction: $\mathrm{Zn\,(s) + 2\,Ag^+\,(aq)} \rightleftharpoons \mathrm{Zn^{2+}\,(aq) + 2\,Ag\,(s)} \quad E^\circ_{cell} = 1.56\ V$

Use Nernst equation to calculate $[\mathrm{Ag^+}]$:

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$$

$$1.54\,V = 1.56\,V - \frac{8.314\frac{J}{mol\cdot K}(298\,K)}{2(96485\,C/mol)}\ln Q$$

$$\ln Q = 1.5577$$

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2} = \frac{2.00}{[\mathrm{Ag^+}]^2} = 4.748$$

$$[\mathrm{Ag^+}] = 0.6\ M$$

Exercise $11.E.21$**

From the cell notation, $\mathrm{Co\,(s)}$ is at the anode (left), meaning it is oxidized. $\mathrm{Fe^{3+}}$ is reduced (right).

This also agrees with standard reduction potentials: $\mathrm{Fe^{3+}}$ has a higher reduction potential than $\mathrm{Co^{2+}}$, so $\mathrm{Fe^{3+}}$ is reduced and cobalt metal is oxidized.

$\mathrm{2\,Fe^{3+}\,(aq) + Co\,(s)} \rightleftharpoons \mathrm{2\,Fe^{2+}\,(aq) + Co^{2+}\,(aq)}$

Determine E°_{cell}.

$E^\circ_{cell} = 0.28\ V + 0.77\ V = 1.05\ V$

$$Q = \frac{[\mathrm{Co^{2+}}][\mathrm{Fe^{2+}}]^2}{[\mathrm{Fe^{3+}}]^2} = \frac{(0.6)(0.9)^2}{(1.0)^2} = 0.486$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$$

$$E_{cell} = 1.05\,V - \frac{8.314\frac{J}{mol\cdot K}(298\,K)}{2(96485\,C/mol)}\ln(0.486) = 1.06\,V$$

Exercise $11.E.22$**

Since both half-cells use the $\mathrm{Cu^{2+}/Cu}$ couple, the standard cell potential is 0 V. However, the cell generates a voltage because the concentrations of $\mathrm{Cu^{2+}}$ are

different in the two half-cells.

Oxidation occurs in the less concentrated solution (0.010 M), while reduction occurs in the more concentrated solution (0.10 M), as the cell spontaneously works to equalize concentrations.

The overall process is:

$\mathrm{Cu^{2+}\,(aq, 0.10M)} \rightarrow \mathrm{Cu^{2+}\,(aq, 0.010M)} \quad Q = \frac{[\mathrm{Cu^{2+}}]_{\mathrm{dilute}}}{[\mathrm{Cu^{2+}}]_{\mathrm{conc}}} = \frac{0.010}{0.10} = 0.10$

Each $\mathrm{Cu^{2+}/Cu}$ half-reaction involves two electrons transferred per copper ion:
$\mathrm{Cu^{2+}\,(aq) + 2\,e^- \longrightarrow Cu\,(s)}$

Even though the electrodes are identical, the electron transfer through the external circuit still involves 2 electrons per $\mathrm{Cu^{2+}}$ ion reduced or oxidized, so we use n = 2 in the Nernst equation.

$$E_{cell} = 0\,V - \frac{8.314\frac{J}{mol\cdot K}(298K)}{2(96485\,C/mol)}\ln(0.10) = 0.030\,V$$

The positive cell potential confirms that the spontaneous direction is from the more concentrated to the less concentrated half-cell.

Exercise $11.E.23$***

$E^\circ_{cell} = 0.28\ V - 0.26\ V = 0.020\ V$

a)

$$Q = \frac{[\mathrm{Co^{2+}}]}{[\mathrm{Ni^{2+}}]} = \frac{(0.010)}{(0.20)} = 0.050$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$$

$$E_{cell} = 0.020\,V - \frac{8.314\frac{J}{mol\cdot K}(298\,K)}{2(96485\,C/mol)}\ln(0.050) = 0.058\,V$$

The reaction will proceed in the forward direction

b) When the battery is dead, the redox reaction is at equilibrium. We can find the equilibrium concentration:

$$E^\circ_{cell} = \frac{RT}{nF}\ln K \quad \rightarrow \quad \ln K = \frac{nFE^\circ_{cell}}{RT}$$

$$\ln K = \frac{(2)(96485\,C/mol)(0.020\,V)}{(8.314\frac{J}{mol\cdot K})(298\,K)} = 1.56$$

$$K = e^{1.56} = 4.7$$

	$Co(s)$ +	$Ni^{2+}(aq)$ ⇌	$Co^{2+}(aq)$	+ Ni(s)
Initial	-	0.20 M	0.010 M	-
Change	-	-x	+x	-
Equilibrium	-	0.20 - x	0.010 + x	-

$$K = \frac{[\mathrm{Co^{2+}}]}{[\mathrm{Ni^{2+}}]} = \frac{(0.010 + x)}{(0.20 - x)} = 4.7$$

$$0.010 + x = 0.94 - 4.7x$$

$$x = 0.16\,M$$

Equilibrium concentrations: $[\mathrm{Ni^{2+}}]$ = 0.04 M and $[\mathrm{Co^{2+}}]$ = 0.17 M.

Exercise $11.E.24$*

A lower (more negative) reduction potential means the metal ion is less easily reduced and the metal itself is more easily oxidized and more likely to corrode.

- Ca is more easily oxidized than Mg.
- Pb is more easily oxidized than Au.
- Zn is more easily oxidized than Fe.
- Ag is more easily oxidized than Pt.

Exercise $11.E.25$**

A sacrificial anode must be more easily oxidized than iron to protect it. A lower (more negative) reduction potential means the metal ion is less easily reduced and the metal itself is more easily oxidized than iron, allowing it to corrode preferentially and protect the steel.

Magnesium and zinc are suitable sacrificial anodes for the steel storage tank because the reduction potential of their ions is lower (more negative) than the reduction potential for $\mathrm{Fe^{2+}}$.

Gold, silver, and nickel ions have higher (less negative) reduction potentials compared to $\mathrm{Fe^{2+}}$, so gold, silver and nickel are less easily oxidized than iron. They will not serve as sacrificial anodes in this application.

Exercise $11.E.26$**

Cathode (reduction):

$$\mathrm{Al^{3+}\,(l) + 3\,e^- \longrightarrow Al\,(l)} \quad E^\circ_{\mathrm{red}} = -1.66\,\mathrm{V}$$

Anode (oxidation):
Reverse the reduction of chlorine:

$$\mathrm{2\,Cl^-\,(l) \longrightarrow Cl_2\,(g) + 2\,e^-} \quad E^\circ_{\mathrm{ox}} = -1.36\,\mathrm{V}$$

Calculating E°_{cell}:
Using $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{ox}} + E^\circ_{\mathrm{red}}$, we get:

$$E^\circ_{\mathrm{cell}} = (-1.36\,\mathrm{V}) + (-1.66\,\mathrm{V}) = -3.02\,\mathrm{V}$$

The negative cell potential shows the reaction is non-spontaneous under standard conditions and requires an external voltage greater than 3.02 V to drive the electrolysis of molten $\mathrm{AlCl_3}$.

Industrial Context:

This process is used in the Hall-Héroult process for aluminum production, where molten $\mathrm{Al_2O_3}$ dissolved in molten cryolite or molten $\mathrm{AlCl_3}$ is electrolyzed to produce aluminum metal at the cathode and chlorine gas at the anode. The required high temperatures and external voltage make aluminum production energy-intensive.

Exercise $11.E.27$**

Calculate the total charge passed:

$$Q = I \times t = (25.0\,\mathrm{C/s})(4.00\,\mathrm{h})\left(\frac{60\,\mathrm{min}}{\mathrm{h}}\right)\left(\frac{60\,\mathrm{s}}{\mathrm{min}}\right) = 360000\,\mathrm{C}$$

Calculate moles of electrons:

$$n_{e^-} = \frac{Q}{F} = \frac{360000\,\mathrm{C}}{96485\,\mathrm{C/mol}} = 3.731\,\mathrm{mol\ e^-}$$

a) Mass of aluminum produced:

Half-reaction: $\mathrm{Al^{3+} + 3\,e^- \longrightarrow Al\,(l)}$

Mass of Al produced:

$$3.731\,\mathrm{mol\ e^-}\left(\frac{1\,\mathrm{mol\ Al}}{3\,\mathrm{mol\ e^-}}\right)\left(\frac{26.98\,\mathrm{g}}{\mathrm{mol}}\right) = 33.6\,\mathrm{g}$$

b) Volume of $\mathrm{Cl_2}$ produced

Anode half-reaction: $\mathrm{2\,Cl^- \longrightarrow Cl_2\,(g) + 2\,e^-}$

$$3.731\,\mathrm{mol\ e^-}\left(\frac{1\,\mathrm{mol\ Cl_2}}{2\,\mathrm{mol\ e^-}}\right)\left(\frac{22.4\,\mathrm{L}}{\mathrm{mol}}\right) = 41.8\,\mathrm{L}$$

Exercise $11.E.28$**

Each mole of Pb requires 2 mol of electrons to plate.

Calculate the mass of Pb re-plated on the cathode using:

$$\text{mass Pb} = (4.50\,\mathrm{C/s})(8.00\,\mathrm{h})(3600\,\mathrm{s/h}) \times \frac{1\,\mathrm{mol\ e^-}}{96485\,\mathrm{C}} \times \frac{1\,\mathrm{mol\ Pb}}{2\,\mathrm{mol\ e^-}} \times 207.2\,\mathrm{g/mol\ Pb} = 139\,\mathrm{g}$$

Exercise $11.E.29$***

We can determine the overall reaction in two ways:

- From the cell notation, oxidation occurs at the left-hand electrode ($\mathrm{Pt\,(s)\ |\ H_2\,(g)\ |\ H^+\,(aq)}$) and reduction occurs at the right-hand electrode ($\mathrm{Ag^+\,(aq)\ |\ Ag\,(s)}$). This means hydrogen gas is oxidized and silver ions are reduced.
- From standard reduction potentials, $\mathrm{Ag^+}$ has a higher reduction potential than $\mathrm{H^+}$, so silver ions will be reduced at the cathode, and hydrogen gas will be oxidized at the anode.

Therefore, the overall reaction is:

$\mathrm{H_2\,(g) + 2\,Ag^+\,(aq) \rightleftharpoons 2\,H^+\,(aq) + 2\,Ag\,(s)}$

Calculate the standard cell potential:

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{ox}} + E^\circ_{\mathrm{red}} = (0.00\,\mathrm{V}) + (0.80\,\mathrm{V}) = 0.80\,\mathrm{V}$$

Apply the Nernst equation:

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$$

$$1.01\,\mathrm{V} = 0.80\,\mathrm{V} - \frac{8.314\frac{J}{mol\cdot K}(298\,K)}{2(96485\,C/mol)}\ln Q$$

$$\ln Q = -16.35 \quad \Rightarrow \quad Q = 7.88 \times 10^{-8}$$

$$Q = \frac{[\mathrm{H^+}]^2}{[\mathrm{Ag^{+2}}]P_{\mathrm{H_2}}} = \frac{[\mathrm{H^+}]^2}{(1.00)^2(1.00)} = 7.88 \times 10^{-8}$$

$$[\mathrm{H^+}] = 2.81 \times 10^{-4}\,\mathrm{M}$$

$$\mathrm{pH} = -\log(2.81 \times 10^{-4}) = 3.55$$

Exercise $11.E.30$***

The reaction is spontaneous when $E_{\mathrm{cell}} > 0$.

Half-reactions:

- Anode (oxidation): $\mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq) + 2\,e^-}$ $\quad E^\circ_{\mathrm{ox}} = -0.34\ \mathrm{V}$
- Cathode (reduction): $\mathrm{Ag^+\,(aq) + e^- \longrightarrow Ag\,(s)}$ $\quad E^\circ_{\mathrm{red}} = +0.80\ \mathrm{V}$

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{ox}} + E^\circ_{\mathrm{red}} = (-0.34\,\mathrm{V}) + (+0.80\,\mathrm{V}) = +0.46\,\mathrm{V}$$

Using the Nernst equation to find the minimum $[\mathrm{Ag^+}]$ for spontaneity. Set $E_{\mathrm{cell}} = 0$ to find the threshold for spontaneity:

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$$

$$0\,\mathrm{V} = 0.46\,\mathrm{V} - \frac{8.314\frac{J}{mol\cdot K}(298\,K)}{2(96485\,C/mol)}\ln Q$$

$$\ln Q = 35.83 \quad \Rightarrow \quad Q = 3.6 \times 10^{15}$$

$$Q = \frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Ag^+}]^2} = \frac{1.00}{[\mathrm{Ag^+}]^2} = 3.6 \times 10^{15}$$

$$[\mathrm{Ag^+}] = 1.7 \times 10^{-8}\,\mathrm{M}$$

The minimum [Ag^+] required for the reaction to be spontaneous in the forward direction when [Cu^{2+}] = 1.00 M is 1.7 × 10^{-8} M.

Exercise $11.E.31$***

a) From the cell notation, oxidation occurs at the left-hand electrode ($Fe(s) \mid Fe^{2+}(aq)$) and reduction occurs at the right-hand electrode ($Cd^{2+}(aq) \mid Cd(s)$). This means:

- Iron metal is oxidized to Fe^{2+}at the anode.
- Cadmium ions are reduced to cadmium metal at the cathode.

This also makes sense based on standard reduction potentials:

- Cd^{2+} has a higher (less negative) reduction potential than Fe^{2+}, so cadmium ions are more easily reduced than iron ions.

Therefore, the overall reaction is:

Reaction: $Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = (+0.45\,V) + (-0.40\,V) = 0.05\,V$$

b) Cell potential under non-standard conditions:

Reaction: $Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

$$Q = \frac{[Fe^{2+}]}{[Cd^{2+}]} = \frac{0.10}{1.00} = 0.10$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q = 0.05\,V - \frac{8.314\frac{J}{mol\cdot K}(298\,K)}{2(96485\,C/mol)}\ln(0.10) = 0.08\,V$$

c) Equilibrium constant K:

At equilibrium, $E_{cell} = 0$:

$$\ln K = \frac{nF}{RT}E^\circ_{cell}$$
$$\ln K = \frac{2(96485\,C/mol)}{8.314\frac{J}{mol\cdot K}(298\,K)}(0.05\,J/C) = 3.89$$
$$K = 49$$

d) Equilibrium concentrations:

	Fe(s) +	Cd^{2+}(aq) ⇌	Fe^{2+}(aq)	+ Cd(s)
Initial	-	1.00 M	0.10 M	-
Change	-	-	+x	-
Equilibrium	-	1.00 - x	0.10 + x	-

$$K = \frac{[Fe^{2+}]}{[Cd^{2+}]} = \frac{0.10 + x}{1.00 - x} = 49$$
$$0.10 + x = 49 - 49x$$
$$50x = 48.9$$
$$x = 0.98\,M$$

[Cd^{2+}] = 0.02 M; [Fe^{2+}] = 1.08 M

e) For each moles of Cd^{2+} that reacts, one mole of $Cd(s)$ is deposited on the electrode.

moles of Cd^{2+} reacted: 0.98 mol/L (1.00 L) = 0.98 mol Cd^{2+}

0.98 mol Cd deposited ⇒ 0.98 mol (112.4 g/mol) = 110 g Cd

f) Equilibrium is reached when 0.98 mol of Cd^{2+} reacts.

n = 2 mol electrons per mol Cd^{2+}.

Total charge required:

$$Q = nFmoles = 2 \times 96485\,C/mol \times 0.98\,mol = 189111\,C$$

We need to calculate time required with 0.50 A current. Using $I = Q/t$:

$$t = \frac{Q}{I} = \frac{189111\,C}{0.50\,C/s} = 3.78 \times 10^5\,s = 105\,hours$$

Exercise $11.E.32$**

When two different metals are in contact in the presence of an electrolyte (like water), they form a galvanic cell. The metal whose metal ion/metal half-reaction has the lower (more negative) standard reduction potential will oxidize (corrode) first, protecting the other metal, which acts as the cathode.

Relevant standard reduction potentials:

- Zinc (Zn^{2+}/Zn): −0.76 V
- Iron (Fe^{2+}/Fe): −0.45 V
- Copper (Cu^{2+}/Cu): +0.34 V

Case 1: Iron and Zinc

Zinc oxidizes (corrodes) more easily than iron and acts as the anode, while iron is protected as the cathode.

Case 2: Iron and Copper

Iron oxidizes (corrodes) more easily than copper and acts as the anode, while copper is protected as the cathode.

This explains why zinc corrodes to protect iron (as in galvanized steel), while copper accelerates the corrosion of iron when in contact.

Exercise $11.E.33$**

A is the anode where oxidation occurs (electrons are travelling away from A).

; the cathode where reduction occurs (gaining electrons)
Cathode (reduction): $\mathrm{M^+(l) + e^- \rightarrow M(l)}$

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12.1: Standard Thermodynamic Quantities

Standard thermodynamic Quantities for Chemical Substances at 25°C. Source of data: CRC Handbook of Chemistry and Physics,84th Edition (2004).

Aluminum

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Al(s)	0.0	0.0	28.3
Al(g)	330.0	289.4	164.6
$AlCl_3$(s)	−704.2	−628.8	109.3
Al_2O_3(s)	−1675.7	−1582.3	50.9

Barium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Ba(s)	0.0	0.0	62.5
Ba(g)	180.0	146.0	170.2
BaO(s)	−548.0	−520.3	72.1
$BaCO_3$(s)	−1213.0	−1134.4	112.1
$BaSO_4$(s)	−1473.2	−1362.2	132.2

Beryllium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Be(s)	0.0	0.0	9.5
Be(g)	324.0	286.6	136.3
$Be(OH)_2$(s)	−902.5	−815.0	45.5
BeO(s)	−609.4	−580.1	13.8

Bismuth

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Bi(s)	0.0	0.0	56.7
Bi(g)	207.1	168.2	187.0

Bromine

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Br(g)	111.9	82.4	175.0
Br_2(l)	0.0	0.0	152.2
Br^-(aq)	−121.6	−104.0	82.4
Br_2(g)	30.9	3.1	245.5
HBr(g)	−36.3	−53.4	198.7
HBr(aq)	−121.6	−104.0	82.4

Cadmium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Cd(s)	0.0	0.0	51.8
Cd(g)	111.8	—	167.7
$CdCl_2$(s)	−391.5	−343.9	115.3
CdS(s)	−161.9	−156.5	64.9

Calcium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Ca(s)	0.0	0.0	41.6
Ca(g)	177.8	144.0	154.9
$CaCl_2$(s)	−795.4	−748.8	108.4
CaF_2(s)	−1228.0	−1175.6	68.5
$Ca(OH)_2$(s)	−985.2	−897.5	83.4
CaO(s)	−634.9	−603.3	38.1
$CaSO_4$(s)	−1434.5	−1322.0	106.5
$CaCO_3$(s, calcite)	−1207.6	−1129.1	91.7
$CaCO_3$(s, aragonite)	−1207.8	−1128.2	88.0

Carbon

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
C(s, graphite)	0.0	0.0	5.7
C(s, diamond)	1.9	2.9	2.4
C(s, fullerene—C_{60})	2327.0	2302.0	426.0
C(s, fullerene—C_{70})	2555.0	2537.0	464.0
C(g)	716.7	671.3	158.1
C(g, fullerene—C_{60})	2502.0	2442.0	544.0
C(g, fullerene—C_{70})	2755.0	2692.0	614.0
CBr_4(s)	29.4	47.7	212.5
CBr_4(g)	83.9	67.0	358.1
CCl_2F_2(g)	−477.4	−439.4	300.8
CCl_2O(g)	−219.1	−204.9	283.5
CCl_4(l)	−128.2	−62.6	216.2
CCl_4(g)	−95.7	−53.6	309.9
CF_4(g)	−933.6	−888.3	261.6
$CHCl_3$(l)	−134.1	−73.7	201.7
$CHCl_3$(g)	−102.7	6.0	295.7
CH_2Cl_2(l)	−124.2	—	177.8

$CH_2Cl_2(g)$	−95.4	−68.9	270.2
$CH_3Cl(g)$	−81.9	−58.5	234.6
$CH_4(g)$	−74.6	−50.5	186.3
$CH_3COOH(l)$	−484.3	−389.9	159.8
$CH_3OH(l)$	−239.2	−166.6	126.8
$CH_3OH(g)$	−201.0	−162.3	239.9
$CH_3NH_2(l)$	−47.3	35.7	150.2
$CH_3NH_2(g)$	−22.5	32.7	242.9
$CH_3CN(l)$	40.6	86.5	149.6
$CH_3CN(g)$	74.0	91.9	243.4
$CO(g)$	−110.5	−137.2	197.7
$CO_2(g)$	−393.5	−394.4	213.8
$CS_2(l)$	89.0	64.6	151.3
$CS_2(g)$	116.7	67.1	237.8
$C_2H_2(g)$	227.4	209.9	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	−84.0	−32.0	229.2
$C_3H_8(g)$	−103.8	−23.4	270.3
$C_3H_6O_3(s)$ (lactic acid)	−694.1	−522.9	142.3
$C_6H_6(l)$	49.1	124.5	173.4
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_{12}(g)$	-167.2	-0.3	388.82
$C_6H_{12}O_6(s)$ (glucose)	−1273.3	−910.4	212.1
$C_2H_5OH(l)$	−277.6	−174.8	160.7
$C_2H_5OH(g)$	−234.8	−167.9	281.6
$(CH_3)_2O(l)$	−203.3	—	—
$(CH_3)_2O(g)$	−184.1	−112.6	266.4
$CH_3CO_2^-(aq)$	−486.0	−369.3	86.6
n-$C_{12}H_{26}(l)$ (dodecane)	−350.9	28.1	490.6

Cesium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Cs(s)	0.0	0.0	85.2
Cs(g)	76.5	49.6	175.6
CsCl(s)	−443.0	−414.5	101.2

Chlorine

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Cl(g)	121.3	105.3	165.2
Cl_2(g)	0.0	0.0	223.1
Cl^-(aq)	−167.2	−131.2	56.5
HCl(g)	−92.3	−95.3	186.9
HCl(aq)	−167.2	−131.2	56.5
ClF_3(g)	−163.2	−123.0	281.6

Chromium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Cr(s)	0.0	0.0	23.8
Cr(g)	396.6	351.8	174.5
$CrCl_3$(s)	−556.5	−486.1	123.0
CrO_3(g)	−292.9	—	266.2
Cr_2O_3(s)	−1139.7	−1058.1	81.2

Cobalt

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Co(s)	0.0	0.0	30.0
Co(g)	424.7	380.3	179.5
$CoCl_2$(s)	−312.5	−269.8	109.2

Copper

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Cu(s)	0.0	0.0	33.2
Cu(g)	337.4	297.7	166.4
CuCl(s)	−137.2	−119.9	86.2
$CuCl_2$(s)	−220.1	−175.7	108.1
CuO(s)	−157.3	−129.7	42.6
Cu_2O(s)	−168.6	−146.0	93.1
CuS(s)	−53.1	−53.6	66.5
Cu_2S(s)	−79.5	−86.2	120.9
CuCN(s)	96.2	111.3	84.5

Fluorine

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
F(g)	79.4	62.3	158.8
F^-(aq)	−332.6	−278.8	−13.8
F_2(g)	0.0	0.0	202.8

HF(g)	−273.3	−275.4	173.8
HF(aq)	−332.6	−278.8	−13.8

Hydrogen

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
H(g)	218.0	203.3	114.7
H_2(g)	0.0	0.0	130.7
H^+(aq)	0.0	0.0	0.0

Iodine

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
I(g)	106.8	70.2	180.8
I^-(aq)	−55.2	−51.6	111.3
I_2(s)	0.0	0.0	116.1
I_2(g)	62.4	19.3	260.7
HI(g)	26.5	1.7	206.6
HI(aq)	−55.2	−51.6	111.3

Iron

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Fe(s)	0.0	0.0	27.3
Fe(g)	416.3	370.7	180.5
Fe^{2+}(aq)	−89.1	−78.9	−137.7
Fe^{3+}(aq)	−48.5	−4.7	−315.9
$FeCl_2$(s)	−341.8	−302.3	118.0
$FeCl_3$(s)	−399.5	−334.0	142.3
FeO(s)	−272.0	−251.4	60.7
Fe_2O_3(s)	−824.2	−742.2	87.4
Fe_3O_4(s)	−1118.4	−1015.4	146.4
FeS_2(s)	−178.2	−166.9	52.9
$FeCO_3$(s)	−740.6	−666.7	92.9

Lead

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Pb(s)	0.0	0.0	64.8
Pb(g)	195.2	162.2	175.4
PbO(s, red or litdarge)	−219.0	−188.9	66.5
PbO(s, yellow or massicot)	−217.3	−187.9	68.7
PbO_2(s)	−277.4	−217.3	68.6

$PbCl_2(s)$	−359.4	−314.1	136.0
PbS(s)	−100.4	−98.7	91.2
$PbSO_4(s)$	−920.0	−813.0	148.5
$PbCO_3(s)$	−699.1	−625.5	131.0
$Pb(NO_3)_2(s)$	−451.9	—	—
$Pb(NO_3)_2(aq)$	−416.3	−246.9	303.3

Lithium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Li(s)	0.0	0.0	29.1
Li(g)	159.3	126.6	138.8
$Li^+(aq)$	−278.5	−293.3	13.4
LiCl(s)	−408.6	−384.4	59.3
$Li_2O(s)$	−597.9	−561.2	37.6

Magnesium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Mg(s)	0.0	0.0	32.7
Mg(g)	147.1	112.5	148.6
$Mg^{2+}(aq)$	-466.85	-454.8	-138.1
$MgCl_2(s)$	−641.3	−591.8	89.6
MgO(s)	−601.6	−569.3	27.0
$Mg(OH)_2(s)$	−924.5	−833.5	63.2
$MgSO_4(s)$	−1284.9	−1170.6	91.6
MgS(s)	−346.0	−341.8	50.3

Manganese

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Mn(s)	0.0	0.0	32.0
Mn(g)	280.7	238.5	173.7
$MnCl_2(s)$	−481.3	−440.5	118.2
MnO(s)	−385.2	−362.9	59.7
$MnO_2(s)$	−520.0	−465.1	53.1
$KMnO_4(s)$	−837.2	−737.6	171.7
$MnO_4^-(aq)$	−541.4	−447.2	191.2

Mercury

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Hg(l)	0.0	0.0	75.9

Hg(g)	61.4	31.8	175.0
$HgCl_2$(s)	−224.3	−178.6	146.0
Hg_2Cl_2(s)	−265.4	−210.7	191.6
HgO(s)	−90.8	−58.5	70.3
HgS(s, red)	−58.2	−50.6	82.4
Hg_2(g)	108.8	68.2	288.1

Molybdenum

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Mo(s)	0.0	0.0	28.7
Mo(g)	658.1	612.5	182.0
MoO_2(s)	−588.9	−533.0	46.3
MoO_3(s)	−745.1	−668.0	77.7

Nickel

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Ni(s)	0.0	0.0	29.9
Ni(g)	429.7	384.5	182.2
$NiCl_2$(s)	−305.3	−259.0	97.7
$Ni(OH)_2$(s)	−529.7	−447.2	88.0

Nitrogen

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
N(g)	472.7	455.5	153.3
N_2(g)	0.0	0.0	191.6
NH_3(g)	−45.9	−16.4	192.8
NH_4^+(aq)	−132.5	−79.3	113.4
N_2H_4(l)	50.6	149.3	121.2
N_2H_4(g)	95.4	159.4	238.5
NH_4Cl(s)	−314.4	−202.9	94.6
NH_4OH(l)	−361.2	−254.0	165.6
NH_4NO_3(s)	−365.6	−183.9	151.1
$(NH_4)_2SO_4$(s)	−1180.9	−901.7	220.1
NO(g)	91.3	87.6	210.8
NO_2(g)	33.2	51.3	240.1
N_2O(g)	81.6	103.7	220.0
N_2O_4(l)	−19.5	97.5	209.2
N_2O_4(g)	11.1	99.8	304.4

HNO_2(g)	−79.5	−46.0	254.1
HNO_3(l)	−174.1	−80.7	155.6
HNO_3(g)	−133.9	−73.5	266.9
HNO_3(aq)	−207.4	−111.3	146.4
NF_3(g)	−132.1	−90.6	260.8
HCN(l)	108.9	125.0	112.8
HCN(g)	135.1	124.7	201.8

Osmium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Os(s)	0.0	0.0	32.6
Os(g)	791.0	745.0	192.6
OsO_4(s)	−394.1	−304.9	143.9
OsO_4(g)	−337.2	−292.8	293.8

Oxygen

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
O(g)	249.2	231.7	161.1
O_2(g)	0.0	0.0	205.2
O_3(g)	142.7	163.2	238.9
OH^-(aq)	−230.0	−157.2	−10.8
H_2O(l)	−285.8	−237.1	70.0
H_2O(g)	−241.8	−228.6	188.8
H_2O_2(l)	−187.8	−120.4	109.6
H_2O_2(g)	−136.3	−105.6	232.7

Phosphorus

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
P(s, white)	0.0	0.0	41.1
P(s, red) −17.6	−17.6	−12.5	22.8
P(s, black)	−39.3	—	—
P(g, white)	316.5	280.1	163.2
P_2(g)	144.0	103.5	218.1
P_4(g)	58.9	24.4	280.0
PCl_3(l)	−319.7	−272.3	217.1
PCl_3(g)	−287.0	−267.8	311.8
$POCl_3$(l)	−597.1	−520.8	222.5
$POCl_3$(g)	−558.5	−512.9	325.5
PCl_5(g)	−374.9	−305.0	364.6

$PH_3(g)$	5.4	13.5	210.2
$H_3PO_4(s)$	−1284.4	−1124.3	110.5
$H_3PO_4(l)$	−1271.7	−1123.6	150.8

Potassium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
K(s)	0.0	0.0	64.7
K(g)	89.0	60.5	160.3
KBr(s)	−393.8	−380.7	95.9
KCl(s)	−436.5	−408.5	82.6
$KClO_3(s)$	−397.7	−296.3	143.1
$K_2O(s)$	−361.5	−322.1	94.1
$K_2O_2(s)$	−494.1	−425.1	102.1
$KNO_2(s)$	−369.8	−306.6	152.1
$KNO_3(s)$	−494.6	−394.9	133.1
KSCN(s)	−200.2	−178.3	124.3
$K_2CO_3(s)$	−1151.0	−1063.5	155.5
$K_2SO_4(s)$	−1437.8	−1321.4	175.6

Rubidium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Rb(s)	0.0	0.0	76.8
Rb(g)	80.9	53.1	170.1
RbCl(s)	−435.4	−407.8	95.9

Selenium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Se(s, gray)	0.0	0.0	42.4
Se(g, gray)	227.1	187.0	176.7
$H_2Se(g)$	29.7	15.9	219.0

Silicon

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Si(s)	0.0	0.0	18.8
Si(g)	450.0	405.5	168.0
$SiCl_4(l)$	−687.0	−619.8	239.7
$SiCl_4(g)$	−657.0	−617.0	330.7
$SiH_4(g)$	34.3	56.9	204.6
SiC(s, cubic)	−65.3	−62.8	16.6
SiC(s, hexagonal)	−62.8	−60.2	16.5

Silver

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Ag(s)	0.0	0.0	42.6
Ag(g)	284.9	246.0	173.0
Ag^+(aq)	105.6	77.1	72.7
AgBr(s)	−100.4	−96.9	107.1
AgCl(s)	−127.0	−109.8	96.3
$AgNO_3$(s)	−124.4	−33.4	140.9
Ag_2O(s)	−31.1	−11.2	121.3
Ag_2S(s)	−32.6	−40.7	144.0

Sodium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Na(s)	0.0	0.0	51.3
Na(g)	107.5	77.0	153.7
Na^+(aq)	−240.1	−261.9	59.0
NaF(s)	−576.6	−546.3	51.1
NaF(aq)	−572.8	−540.7	45.2
NaCl(s)	−411.2	−384.1	72.1
NaCl(aq)	−407.3	−393.1	115.5
NaBr(s)	−361.1	−349.0	86.8
NaBr(g)	−143.1	−177.1	241.2
NaBr(aq)	−361.7	−365.8	141.4
NaO_2(s)	−260.2	−218.4	115.9
Na_2O(s)	−414.2	−375.5	75.1
Na_2O_2(s)	−510.9	−447.7	95.0
NaCN(s)	−87.5	−76.4	115.6
$NaNO_3$(aq)	−447.5	−373.2	205.4
$NaNO_3$(s)	−467.9	−367.0	116.5
NaN_3(s)	21.7	93.8	96.9
Na_2CO_3(s)	−1130.7	−1044.4	135.0
Na_2SO_4(s)	−1387.1	−1270.2	149.6

Sulfur

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
S(s, rhombic)	0.0	0.0	32.1
S(g, rhombic)	277.2	236.7	167.8
SO_2(g)	−296.8	−300.1	248.2

$SO_3(g)$	−395.7	−371.1	256.8
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1
$SOCl_2(g)$	−212.5	−198.3	309.8
$H_2S(g)$	−20.6	−33.4	205.8
$H_2SO_4(aq)$	−909.3	−744.5	20.1

Tin

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Sn(s, white)	0.0	0.0	51.2
Sn(s, gray)	−2.1	0.1	44.1
Sn(g, white)	301.2	266.2	168.5
$SnCl_4(l)$	−511.3	−440.1	258.6
$SnCl_4(g)$	−471.5	−432.2	365.8
$SnO_2(s)$	−557.6	−515.8	49.0

Titanium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Ti(s)	0.0	0.0	30.7
Ti(g)	473.0	428.4	180.3
$TiCl_2(s)$	−513.8	−464.4	87.4
$TiCl_3(s)$	−720.9	−653.5	139.7
$TiCl_4(l)$	−804.2	−737.2	252.3
$TiCl_4(g)$	−763.2	−726.3	353.2
$TiO_2(s)$	−944.0	−888.8	50.6

Uranium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
U(s)	0.0	0.0	50.2
U(g)	533.0	488.4	199.8
$UO_2(s)$	−1085.0	−1031.8	77.0
$UO_2(g)$	−465.7	−471.5	274.6
$UF_4(s)$	−1914.2	−1823.3	151.7
$UF_4(g)$	−1598.7	−1572.7	368.0
$UF_6(s)$	−2197.0	−2068.5	227.6
$UF_6(g)$	−2147.4	−2063.7	377.9

Vanadium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
V(s)	0.0	0.0	28.9

V(g)	514.2	754.4	182.3
VCl_3(s)	−580.7	−511.2	131.0
VCl_4(l)	−569.4	−503.7	255.0
VCl_4(g)	−525.5	−492.0	362.4
V_2O_5(s)	−1550.6	−1419.5	131.0

Zinc

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Zn(s)	0.0	0.0	41.6
Zn(g)	130.4	94.8	161.0
$ZnCl_2$(s)	−415.1	−369.4	111.5
$Zn(NO_3)_2$(s)	−483.7	—	—
ZnS(s, sphalerite)	−206.0	−201.3	57.7
$ZnSO_4$(s)	−982.8	−871.5	110.5

Zirconium

Substance	$\Delta_f H^\circ$ (kJ/mol)	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)
Zr(s)	0.0	0.0	39.0
Zr(g)	608.8	566.5	181.4
$ZrCl_2$(s)	−502.0	−386	110
$ZrCl_4$(s)	−980.5	−889.9	181.6

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12.2: Bond Energies

Table 12.2.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H−H	436	C−S	260	F−Cl	255
H−C	415	C−Cl	330	F−Br	235
H−N	390	C−Br	275	Si−Si	230
H−O	464	C−I	240	Si−P	215
H−F	569	N−N	160	Si−S	225
H−Si	395	N=N	418	Si−Cl	359
H−P	320	N≡N	946	Si−br	290
H−S	340	N−O	200	Si−I	215
H−Cl	432	N−F	270	P−P	215
H−Br	370	N−P	210	P−S	230
H−I	295	N−Cl	200	P−Cl	330
C−C	345	N−Br	245	P−Br	270
C=C	611	O−O	140	P−I	215
C≡C	837	O=O	498	S−S	215
C−N	290	O−F	160	S−Cl	250
C=N	615	O−Si	370	S−Br	215
C≡N	891	O−P	350	Cl−Cl	243
C−O	350	O−Cl	205	Cl−Br	220
C=O	741	O−I	200	Cl−I	210
C≡O	1080	F−F	160	Br−Br	190
C−F	439	F−Si	540	Br−I	180
C−Si	360	F−P	489	I−I	150
C−P	265	F−S	285		

Table 12.2.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å=0.1 nm)	Bond Energy (kJ/mol)
C−C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C−N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C−O	1.43	350
C=O	1.23	741

Bond	Bond Length (Å=0.1 nm)	Bond Energy (kJ/mol)
$C \equiv O$	1.13	1080

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12.3: Acid Dissociation Constants

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Acetic acid	CH_3CO_2H	1.75×10^{-5}	4.756	-	-	-	-	-	-
Arsenic acid	H_3AsO_4	5.5×10^{-3}	2.26	1.7×10^{-7}	6.76	5.1×10^{-12}	11.29	-	-
Benzoic acid	$C_6H_5CO_2H$	6.25×10^{-5}	4.204	-	-	-	-	-	-
Boric acid	H_3BO_3	5.4×10^{-10}*	9.27*	>1×10^{-14}*	>14*	-	-	-	-
Bromoacetic acid	CH_2BrCO_2H	1.3×10^{-3}	2.90	-	-	-	-	-	-
Carbonic acid	H_2CO_3	4.5×10^{-7}	6.35	4.7×10^{-11}	10.33	-	-	-	-
Chloroacetic acid	CH_2ClCO_2H	1.3×10^{-3}	2.87	-	-	-	-	-	-
Chlorous acid	$HClO_2$	1.1×10^{-2}	1.94	-	-	-	-	-	-
Chromic acid	H_2CrO_4	1.8×10^{-1}	0.74	3.2×10^{-7}	6.49	-	-	-	-
Citric acid	$C_6H_8O_7$	7.4×10^{-4}	3.13	1.7×10^{-5}	4.76	4.0×10^{-7}	6.40	-	-
Cyanic acid	$HCNO$	3.5×10^{-4}	3.46	-	-	-	-	-	-
Dichloroacetic acid	$CHCl_2CO_2H$	4.5×10^{-2}	1.35	-	-	-	-	-	-
Fluoroacetic acid	CH_2FCO_2H	2.6×10^{-3}	2.59	-	-	-	-	-	-
Formic acid	CH_2O_2	1.8×10^{-4}	3.75	-	-	-	-	-	-
Hydrazoic acid	HN_3	2.5×10^{-5}	4.6	-	-	-	-	-	-
Hydrocyanic acid	HCN	6.2×10^{-10}	9.21	-	-	-	-	-	-
Hydrofluoric acid	HF	6.3×10^{-4}	3.20	-	-	-	-	-	-
Hydrogen peroxide	$HOOH$	2.0×10^{-12}	11.7						
Hydrogen selenide	H_2Se	1.3×10^{-4}	3.89	1.0×10^{-11}	11.0	-	-	-	-
Hydrogen sulfide	H_2S	8.9×10^{-8}	7.05	1×10^{-19}	19	-	-	-	-
Hydrogen telluride	H_2Te	2.5×10^{-3}‡	2.6‡	1×10^{-11}	11	-	-	-	-
Hypobromous acid	$HBrO$	2.8×10^{-9}	8.55	-	-	-	-	-	-
Hypochlorous acid	$HClO$	4.0×10^{-8}	7.40	-	-	-	-	-	-
Hypoiodous acid	HIO	3.2×10^{-11}	10.5	-	-	-	-	-	-
Iodic acid	HIO_3	1.7×10^{-1}	0.78	-	-	-	-	-	-
Iodoacetic acid	CH_2ICO_2H	6.6×10^{-4}	3.18	-	-	-	-	-	-
Nitrous acid	HNO_2	5.6×10^{-4}	3.25	-	-	-	-	-	-
*** Measured at 20°C, not 25°C.**									
‡ Measured at 18°C, not 25°C.									

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Oxalic acid	$C_2H_2O_4$	5.6×10^{-2}	1.25	1.5×10^{-4}	3.81	-	-	-	-
Periodic acid	HIO_4	2.3×10^{-2}	1.64	-	-	-	-	-	-
Phenol	C_6H_5OH	1.0×10^{-10}	9.99	-	-	-	-	-	-
Phosphoric acid	H_3PO_4	6.9×10^{-3}	2.16	6.2×10^{-8}	7.21	4.8×10^{-13}	12.32	-	-
Phosphorous acid	H_3PO_3	5.0×10^{-2}*	1.3*	2.0×10^{-7}*	6.70*	-	-	-	-
Pyrophosphoric acid	$H_4P_2O_7$	1.2×10^{-1}	0.91	7.9×10^{-3}	2.10	2.0×10^{-7}	6.70	4.8×10^{-10}	9.32
Resorcinol	$C_6H_4(OH)_2$	4.8×10^{-10}	9.32	7.9×10^{-12}	11.1	-	-	-	-
Selenic acid	H_2SeO_4	Strong	Strong	2.0×10^{-2}	1.7	-	-	-	-
Selenious acid	H_2SeO_3	2.4×10^{-3}	2.62	4.8×10^{-9}	8.32	-	-	-	-
Sulfuric acid	H_2SO_4	Strong	Strong	1.0×10^{-2}	1.99	-	-	-	-
Sulfurous acid	H_2SO_3	1.4×10^{-2}	1.85	6.3×10^{-8}	7.2	-	-	-	-
meso-Tartaric acid	$C_4H_6)O_6$	6.8×10^{-4}	3.17	1.2×10^{-5}	4.91	-	-	-	-
Telluric acid	H_2TeO_4	2.1×10^{-8}‡	7.68‡	1.0×10^{-11}‡	11.0‡	-	-	-	-
Tellurous acid	H_2TeO_3	5.4×10^{-7}	6.27	3.7×10^{-9}	8.43	-	-	-	-
Trichloroacetic acid	CCl_3CO_2H	2.2×10^{-1}	0.66	-	-	-	-	-	-
Trifluoroacetic acid	CF_3CO_2H	3.0×10^{-1}	0.52	-	-	-	-	-	-
*** Measured at 20°C, not 25°C.**									
‡ Measured at 18°C, not 25°C.									

Source of data: *CRC Handbook of Chemistry and Physics,* 84th Edition (2004).

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12.4: Standard Reduction Potentials

Table 12.4.1*: Selected Standard Reduction Potentials at 25 °C*

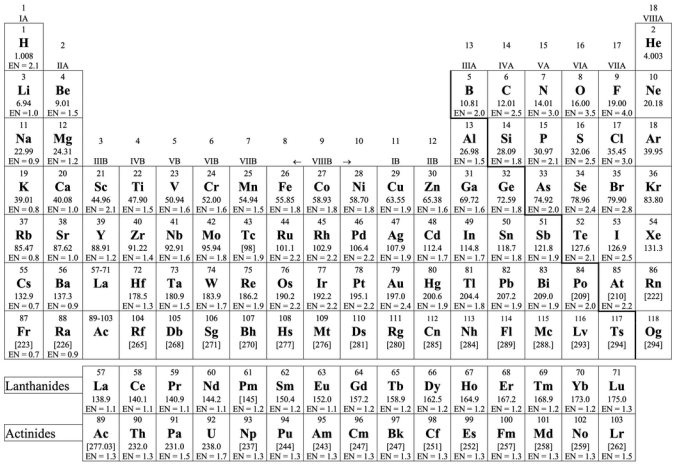
Half-Reaction	E° (V)
$F_2(g) + 2\,e^- \rightarrow 2\,F^-(aq)$	+2.87
$PbO_2(s) + {SO_4}^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \rightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.69
${MnO_4}^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow$ [redacted]$(aq) + 4\,H_2O(l)$	+1.51
$Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)$	+1.36
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	+1.23
$Pt^{2+}(aq) + 2\,e^- \rightarrow Pt(s)$	+1.20
$Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)$	+1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
${Hg_2}^{2+}(aq) + 2\,e^- \rightarrow 2\,Hg(l)$	+0.80
[redacted]$(aq) + e^- \rightarrow$ [redacted](aq)	+0.77
${MnO_4}^-(aq) + 2\,H_2O(l) + 3\,e^- \rightarrow MnO_2(s) + 4\,OH^-(aq)$	+0.56
$I_2(s) + 2\,e^- \rightarrow 2\,I^-(aq)$	+0.54
$NiO_2(s) + 2\,H_2O(l) + 2\,e^- \rightarrow Ni(OH)_2(s) + 2\,OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2\,e^- \rightarrow 2\,Hg(l) + 2\,Cl^-(aq)$	+0.27
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
[redacted]$(aq) + 2\,e^- \rightarrow$ [redacted](aq)	+0.15
$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$	−0.26
$Co^{2+}(aq) + 2\,e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2\,e^- \rightarrow Pb(s) + {SO_4}^{2-}(aq)$	−0.35
$Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$	−0.45
$Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$	−0.74
$Mn^{2+}(aq) + 2\,e^- \rightarrow Mn(s)$	−1.19
$Zn(OH)_2(s) + 2\,e^- \rightarrow Zn(s) + 2\,OH^-(aq)$	−1.25
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71

Half-Reaction	E° (V)
$\mathrm{Ca}^{2+}(aq) + 2\,\mathrm{e}^- \rightarrow \mathrm{Ca}(s)$	−2.87
$\mathrm{Ba}^{2+}(aq) + 2\,\mathrm{e}^- \rightarrow \mathrm{Ba}(s)$	−2.91
$\mathrm{K}^{+}(aq) + \mathrm{e}^- \rightarrow \mathrm{K}(s)$	−2.93
$\mathrm{Li}^{+}(aq) + \mathrm{e}^- \rightarrow \mathrm{Li}(s)$	−3.04

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12.5: Periodic Table



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12.6: CHM 135H Equations and Constants

$$E = h\nu \qquad c = \lambda\nu \qquad PV = nRT$$

$$E_n = \frac{-2.18\times10^{-18}J}{n^2} \qquad \Delta E = -2.18\times10^{-18}J\left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right)$$

$$\overline{E_k} = \frac{3RT}{2N_A} \qquad u_{rms} = \sqrt{\frac{3RT}{M}} \qquad P_A = X_A P_{tot}$$

$$S = k\ln W \qquad E_K = \frac{1}{2}mu^2 \qquad Q = I \times t \qquad Q = moles\,(e^-) \times F$$

$$\Delta H = \Delta E + P\Delta V \qquad \Delta G = \Delta H - T\Delta S \qquad \Delta G = -nFE_{cell}$$

$$\Delta G = \Delta G^o + RT\ln Q \qquad q_{cal} = C_{cal}\Delta T \qquad q = c \times mass \times \Delta T$$

$$\Delta E = q + w \qquad w = -P\Delta V \qquad \text{For: } ax^2 + bx + c = 0\,, \quad x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

$$[A]_t = -kt + [A]_0 \qquad \ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \qquad \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \ln\left(\frac{k_2}{k_1}\right) = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad K_p = K_c(RT)^{\Delta n}$$

$$pH = pK_a + log\left(\frac{[A^-]}{[HA]}\right) \qquad E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q \qquad E_{cell} = E^o_{cell} - \frac{0.0592\,V}{n}log\,Q \;\; at\;25°C$$

Constants	
Avogadro's number	$N_A = 6.022 \times 10^{23}$ mol^{-1}
Mass of an electron	$m_e = 9.109 \times 10^{-31}$ kg
Boltzmann's constant	$k = 1.380658 \times 10^{-23}$ J K^{-1}
Zero point	0 °C = 273.15 K
Gas constant	R = 8.314 J mol^{-1}K^{-1} R = 0.08206 L atm mol^{-1}K^{-1}
Planck's constant	$h = 6.626 \times 10^{-34}$ J s
Speed of light	$c = 3.00\times10^{8}$ m s^{-1}
Ion-product constant of water (at 25 °C)	$K_w = 1 \times 10^{-14}$
Faraday's constant	F = 96485 C mol^{-1}

Conversion factors
1 amu = $1.6605402 \times 10^{-27}$ kg
1 atmosphere (atm) = 1.01325×10^5 Pa = 760.0 mm Hg (torr) = 1.01325 bar
1 calorie (cal) = 4.184 joules (J)
1 m = 10 dm = 100 cm = 10^3 mm = 10^6 µm = 10^9 nm = 10^{12} pm
1 L atm = 101.325 J = 24.217 cal
1 J = 1 kgm^{2}s^{-2}
1 V = 1 J C^{-1}
1 A = 1 C s^{-1}

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12.7: Green Chemistry and Sustainability

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12.7.1: Overview

To be sustainable, we must be able to meet the needs of the present generation without compromising the ability of future generations to meet their own needs.[1] What does this have to do with chemistry? Whether we realize it or not, chemistry is connected to early every aspects of our lives. It helps us grow food, produce clean water, develop medicine, generate energy, manufacture materials and create the technologies we rely on every day. It is hard to think of an area of life that does not depend on chemistry in some way.

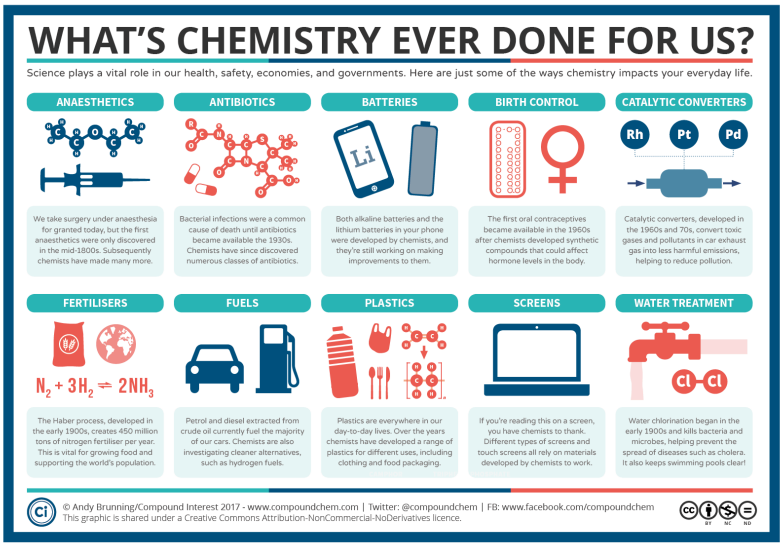


Figure 12.7.1.1: Impact of Chemistry in Everyday Life (Image: "The March for Science – Ten Things That Chemistry Has Done for Us" by Andy Brunning, from Compound Interest (2017), licensed under CC BY-NC-ND 4.0. No changes were made.)

Because chemistry plays such an important role in society, chemists also have an important responsibility. How can we use chemistry to improve our quality of life while ensuring that future generations will still have the resources they need? Answering this question requires us to consider not only human needs, but also the health of our planet. Recognizing the need for a more sustainable future, the United Nations developed the 17 United Nations Sustainability and Development Goals (UNSDGS) as a "shared blueprint for peace and prosperity for people and the planet, now and into the future".[2]



Figure 12.7.1.2: The 17 Sustainable Development Goals (Sustainable Development Goals.png and PDF infographic from un.org, Public domain, via Wikimedia Commons)

Although these goals are broad, chemistry contributes to many of them. Some examples include:

- **SDG #2: Zero Hunger**
  - generation of more effective fertilizers and crop protection
  - enhanced food nutrition and preservation
  - development of food quality and safety tools
- **SDG #3: Good Health and Well-Being**
  - creation of medicines and vaccines
  - development of diagnostic and medical testing
  - improved nutrition and food safety
- **SDG #6: Clean Water and Sanitation**
  - enhanced methods for water purification, especially in remote areas
  - improved water quality testing
  - reduce water pollution
  - development of desalination techniques
- **SDG #7: Affordable and Clean Energy**
  - improved energy efficiency
  - continued development of renewable energy sources (e.g., batteries, biofuels, hydrogen, solar, wind)
- **SDG #9: Industry, Innovation and Infrastructure**
  - improved construction materials (e.g., high-strength steel, corrosion-resistant metals, light-weight composites)
  - enhanced efficiencies of transportation technologies
- **SDG #12: Responsible Consumption and Production**
  - reduce waste and improve recycling
  - development of circular economies
  - use of renewable chemical and fuel sources
  - create safer chemicals
  - generate biodegradable chemicals
- **SDG #13: Climate Action**
  - continued reduction of greenhouse gases
  - carbon capture and storage
  - development of analytical tools to detect air pollution

This list provides some general examples how chemistry can help our society in being more sustainable. In the next section, you will learn

about the 12 Principles of Green Chemistry, which provide practical guidelines for designing chemical products and processes that reduce waste, improve efficiency, and minimize environmental impact. As you study these principles, you will see how they support many of the United Nations Sustainable Development Goals.

Building a more sustainable future will require contributions from many fields, and chemistry will play an essential role. Chemistry not only helps us understand challenges such as climate change, biodiversity loss, and pollution, but also provides the knowledge and tools needed to develop solutions.

References

1. https://www.un.org/en/academic-impact/sustainability
2. https://sdgs.un.org/goals

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12.7.2: Green Chemistry

According to the International Union of Pure and Applied Chemistry (IUPAC), green chemistry is "the invention, design, and application of chemical products and processes to reduce or eliminate the use and generation of hazardous substances."[1] Green chemistry therefore considers not only how chemicals are made, but also how they are used and what happens to them after they have served their purpose.

You may be wondering: *Hasn't chemistry always worked this way?* Not entirely. Traditionally, chemists have focused on developing molecules that perform a specific function, with less emphasis on minimizing waste, reducing hazardous substances, or considering the environmental impact of the manufacturing process and the products themselves. This approach has led to many innovations that society depends on every day, including fertilizers, medicines, and plastics. Today, however, chemists are also working to make these products and processes more sustainable by reducing the use and generation of hazardous substances and minimizing their impact on human health and the environment.

Chemists are increasingly redesigning chemical processes to reduce their environmental impact. One example is the synthesis of Islatravir, an antiviral drug used for HIV treatment and prevention. The original synthesis, reported in 2017, required 16 reaction steps and generated more than 6000 kg of waste for every 1 kg of Islatravir produced. This quantity is measured using product mass intensity (PMI), which compares the total mass of materials used to the mass of the final product. In 2024, chemists at Merck & Co. redesigned this synthesis using biocatalysis, in which enzymes are used as catalysts.[2] The new process reduced the synthesis from 16 steps to just 5 and lowered the PMI from more than 6000 to about 360 kg of waste per kilogram of product, a reduction by a factor of more than 18! In recognition of this achievement, Merck & Co. received the 2025 ACS Green Chemistry Challenge Award in the Greener Synthetic Pathways category.

Fun Fact: The use of enzymes as catalysts is known as biocatalysis and has become an important strategy in modern chemical synthesis. However, naturally occurring enzymes do not always function under the conditions needed for industrial or laboratory reactions. Using a technique called directed evolution, scientists can modify enzymes so that they perform better under these conditions. Prof. Frances Arnold of Caltech is one of the pioneers of directed evolution and was awarded the 2018 Nobel Prize in Chemistry for her contributions to this field.[3]

How can chemists determine whether a chemical process is becoming more sustainable? One useful tool is the 12 Principles of Green Chemistry (GCPs). Developed by Drs. Paul Anastas and John Warner, these principles provide a framework for designing chemical products and processes that are safer, more efficient, and more sustainable.[4] Although they were introduced more than 25 years ago, the principles continue to guide green chemistry research and industrial practice today. The Islatravir synthesis illustrates several of these principles, including the use of catalysis and the prevention of waste.

The following sections introduce each of the 12 principles and explain how they can be applied in practice.

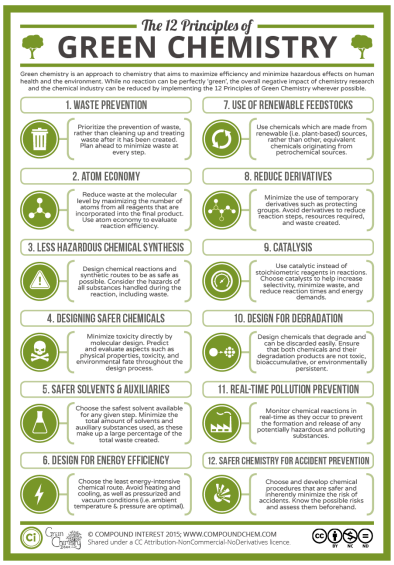


Figure 12.7.2.1: The 12 Principles of Green Chemistry (Compound Interest (2015). Licensed under CC BY-NC-ND 4.0. No changes were made.)

1. **Prevention:** *It is better to prevent waste than to treat or clean up waste after it has been created.*

The easiest way to treat waste is to not make it at all! Designing reactions and processes that use only the materials that are needed helps to reduce the amount of waste that would need to be taken care of afterwards. The amount of waste created in chemical reactions can be measured by the environmental (E) factor.

$$\text{E factor} = \frac{\text{mass of waste (kg)}}{\text{mass of product (kg)}}$$

However, E factor only considers the waste generated from the chemical reaction. After a reaction is completed, the desired product needs to be isolated and purified, and these processes often require a lot of additional chemicals. To evaluate the entire process, another metric called product mass intensity (PMI) that considers all materials used throughout the entire process (reaction, isolation, and purification):

$$\text{Product Mass Intensity} = \frac{\text{total mass of input materials for the chemical process (kg)}}{\text{mass of product (kg)}}$$

Note – for both the E factor and PMI, a "greener" process has a value closer to 1

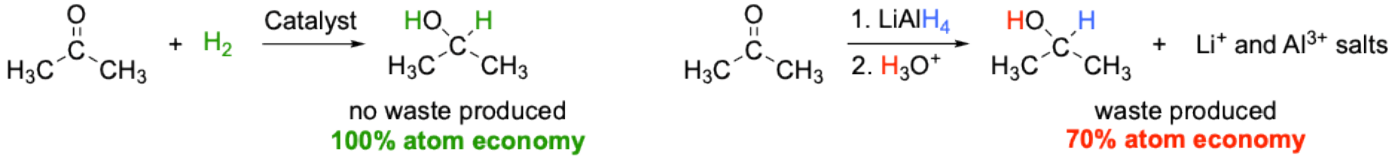
2. **Atom Economy:** *Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.*

This principle is similar to GCP #1, but instead of measuring the amount of waste produced or materials used, it measures how many atoms in our starting materials end up in our product. This concept was first introduced by Prof. B. Trost in 1990 and offers another perspective to assess chemical reactions. Chemical reactions are not only about producing as much of our desired product as possible, but also about ensuring that we use our starting materials efficiently. Atom economy is especially useful because it allows chemists to evaluate the sustainability of a proposed reaction before carrying out any experiments.

$$\text{Atom Economy (AE)} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reactants}} \times 100\%$$

Note - a "greener" process has an AE value closer to 100%

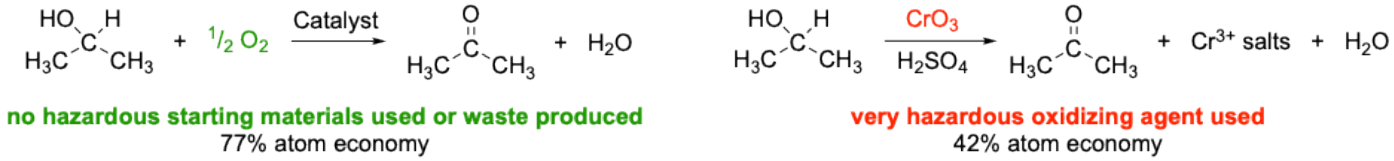
A comparison is shown below for the reduction of a ketone to an alcohol. The use of hydrogen gas and a metal catalyst provide a method where all the starting materials are incorporated into the desired product (100% atom economy). The use of a stoichiometric reducing agent, lithium aluminum hydride ($LiAlH_4$), produces Li^+ and Al^{3+} salts as waste and thus has a lower atom economy (70%). Thus, the metal-catalyzed route provides the "greener" method.



3. **Less Hazardous Chemical Syntheses:** *Synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.*

This principle encourages chemists to consider not only the function of a molecule, but also how it is made. To achieve this, chemists need to consider the possible hazards, in terms of human health and the environment, during the design stage of their experiments. By avoiding hazardous substances from the outset, chemists can reduce or even eliminate the need to manage hazardous waste later! Meeting this principle often requires chemists to develop creative new methods to make molecules.

A comparison is shown below for the oxidation of an alcohol to a ketone. The use of oxygen gas with a metal catalyst provides a method without hazardous starting materials and only water as a waste product. In contrast, the second method uses chromium oxide (CrO_3) which is hemotoxic, genotoxic, and carcinogenic for humans and animals. Therefore, the metal-catalyzed method using oxygen gas is "greener" as it is less much hazardous. This method also provides a better atom economy (GCP #2).



4. **Designing Safer Chemicals:** *Chemical products should be designed to preserve efficacy of function while reducing toxicity.*

Chemists have the incredible ability to design and synthesize new molecules. While this is often very exciting, we often do not understand the potential hazards that these new compounds may pose to human health and the environment. Therefore, it is important for chemists to gain a better understanding of the toxicity of the chemicals that we produce. We can perform tests to determine the toxicity of new compounds or find ways to predict the toxicities of compounds ahead of time, so we can make less toxic materials.

An important example related to hazard is the type of refrigerant gases used in such applications as refrigerators or air conditioners. Natural refrigerants, ammonia (NH_3) and sulfur dioxide (SO_2), were commonly used as refrigerants when household refrigerants were first invented. Accidental leakage of these gases led to deaths due to their toxicities, and as such, these gases were no longer used as refrigerants. In the mid-1900s chemists began to make synthetic alternatives called chlorofluorocarbons (CFCs) but they were found to degrade the earth's ozone layer and thus were banned in the Montreal Protocol in 1987. Hydrofluorocarbons (HFCs) were created to replace CFCs as their ozone depleting abilities were much reduced; however, it been found that HFCs are potent greenhouse gases. The use of HFCs is now being phased out. Hydrofluoroolefins (HFOs) and natural refrigerants are now being explored as possible sustainable alternatives. This example highlights the importance of understanding the long-term consequences to humans and our environment before the large-scale application of chemicals are introduced in our society.

5. **Safer Solvents and Auxiliaries:** *The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when required.*

Most chemical reactions take place in solution, where a liquid chemical, known as a solvent, is added to dissolve all starting materials. Solvents provide the environment in which many chemical reactions occur by dissolving reactants, allowing them to collide, and helping to transfer heat. Although solvents are often essential, they can account for a large fraction of the waste generated during a chemical process. The choice and amount of solvent can greatly influence the sustainability of a chemical reaction. Several chemical companies have made solvent guides that help chemists choose "greener" solvents. Below is an example of a solvent selection to assist chemists in making greener solvent choices that uses a traffic light analogue (green = recommended, yellow = problematic and red = hazardous solvents):

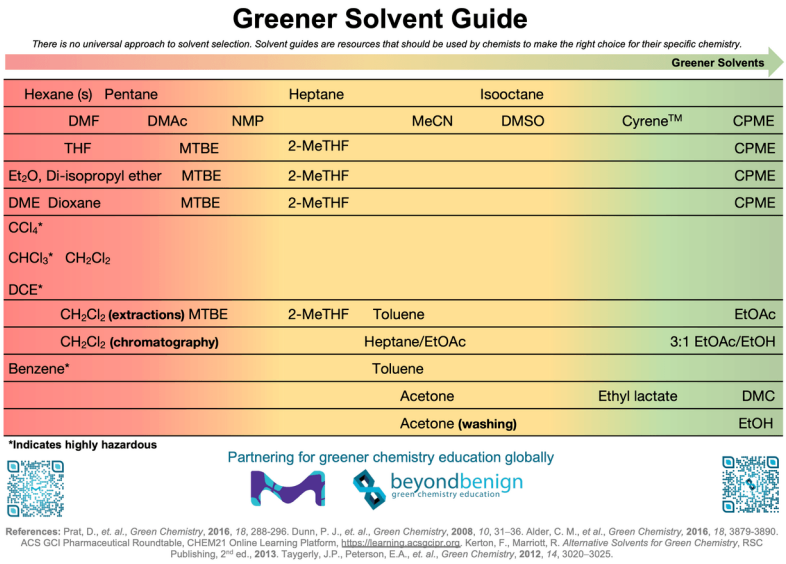


Figure 12.7.2.2: Greener Solvent Guide. (Beyond Benign. Licensed under CC BY-NC-SA 4.0)

6. **Design for Energy Efficiency:** *Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure where possible.*

If we look at the energy plot in Figure 12.7.2.3, we can see that to transform reactants to products, we need some input of energy, even for an exothermic reaction. This energy is most often provided in the form of thermal energy (heat), but we must keep in mind that energy is not free. Much of the world's energy comes from the burning of fossil fuels, which is a major contributor to global warming. Therefore, we should strive to only use as much energy as needed. To reduce energy requirements, we can monitor reactions to stop them when completed (instead of heating them longer than needed), explore other methods to introduce energy into reactions (*e.g.*, light energy, mechanical energy), investigate using catalysts (more on catalysis will be discussed in GCP #9), or using renewable energy sources (*e.g.*, solar, wind).

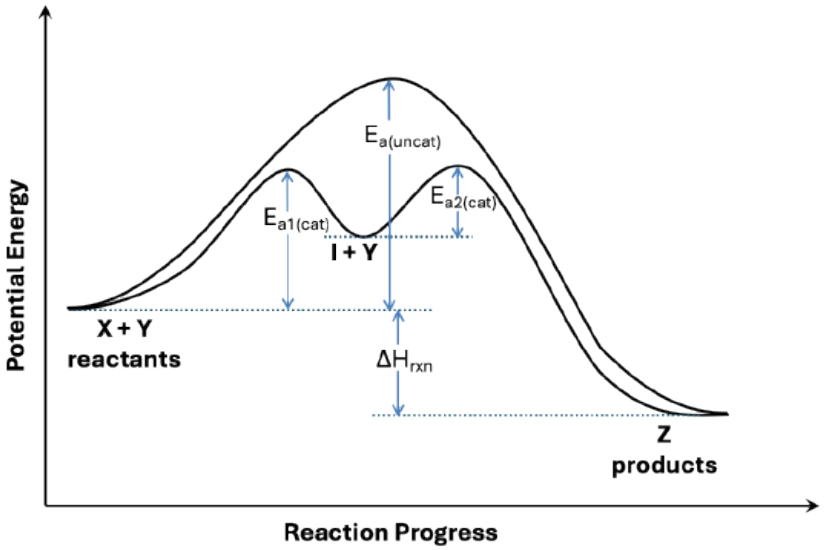


Figure 12.7.2.3: Reaction energy diagram for the uncatalyzed reaction of X + Y ⇾ Z (single step with higher activation energy) and the catalyzed reaction (two steps, lower activation energy). A catalyst increases reaction rate by providing a new reaction pathway with a lower activation energy.

7. **Use of Renewable Feedstocks:** *A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.*

Renewable feedstocks are raw materials derived from resources that can be replenished naturally on a human timescale (*e.g.*, plants, algae, agricultural waste materials) rather than finite fossil resources. Using renewable sources helps reduce dependence on non-renewable resources, lowers the environmental impact of chemical production, and can decrease greenhouse gas emissions when managed sustainably.

Examples include producing second generation bioethanol from lignocellulose feedstocks and manufacturing biodegradable plastics from plant-derived starting materials. This principle supports the development of a more sustainable chemical industry by promoting resource conservation and circular use of materials.

8. **Reduce derivatives:** *Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.*

Ideally, molecules would react exactly how we would like, forming only our desired product and the process would require as little energy and materials as possible. However, this is rarely the case, and we must often take precautions to avoid unwanted reactions from also taking place. For example, if a reagent can react at two possible sites, chemists will add a "protecting group" to prevent a reaction at the undesired site. The reaction sequence involves protection, transformation of interest, and deprotection. These additional protection and deprotection steps require extra reagents, consume energy, and generate additional waste. For example, this is necessary in peptide synthesis due to the two reactive sites on the amino acid (the carboxylic acid and amine). In order to make sure the peptide chain is growing in the right sequence, there is a series of protections and deprotections for *each* amino acid that are needed as seen in Figure 12.7.2.4. Nature often performs remarkably selective reactions without the need for protecting groups because enzymes precisely control which functional groups react. Chemists are starting to learn from nature and are working to incorporate biocatalysis in their syntheses, as highlighted above in the introduction of this section.

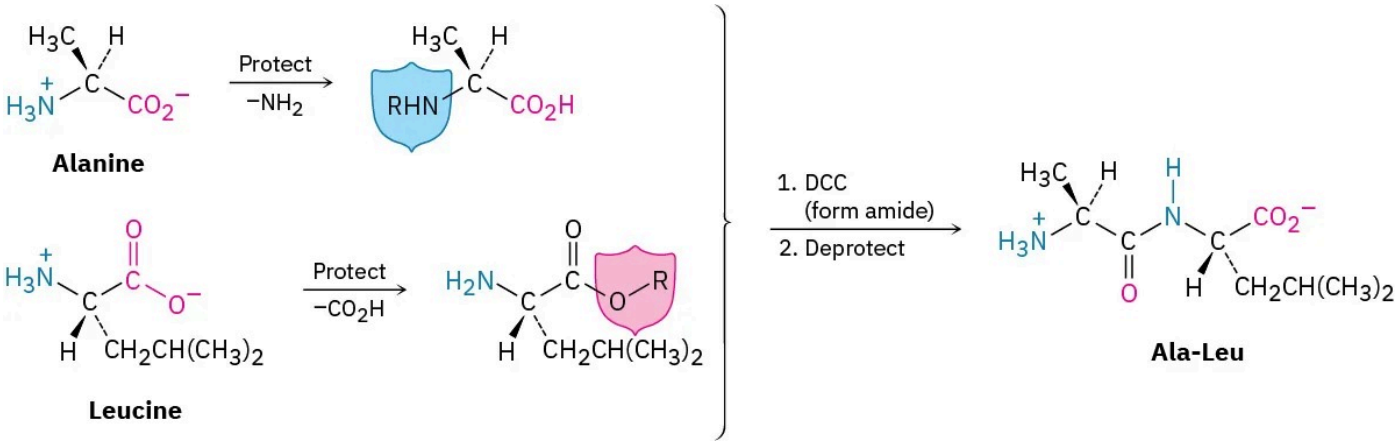


Figure 12.7.2.4: Peptide synthesis using protecting groups. (Image from Organic Chemistry by John McMurry, OpenStax (Section 26.7: Peptide Synthesis), licensed under CC BY-NC-SA 4.0)

9. **Catalysis:** Use of *catalytic reagents instead of stoichiometric reagents to minimize waste production and energy consumption.*

Catalysts are unique reaction components because they decrease the overall activation energy barrier for chemical reactions without being consumed in the process. Depending on the catalyst, it can help to prevent the amount of waste produced (GCP #1), improve the atom economy (GCP #2), enable the reaction to use less energy (GCP #6), and reduce the number of derivatives required for a synthesis (GCP #8)! As we have already seen, catalytic oxidation and reduction reactions can reduce waste, improve atom economy, and lower energy requirements, illustrating how one principle often supports several others.

10. **Design for Degradation:** *Chemical products should be designed so that at the end of their function they break down into non-hazardous chemicals that do not persist in the environment.*

Our discussion so far has focused on how to make chemicals and processes "greener"; however, we need to consider what happens at the end-of-life for our chemicals. GCP #10 asks us to consider what we have made and what its impact will be after it has served its purpose. Consider plastics, for instance, a great material used to transport items such as foods, drinks, clothing, *etc*. The problem is that plastic recycling rates are very low, and tons of plastic pile up in landfills and leach into the environment. Once in the environment, most conventional plastics do not "degrade" (break down into its starting molecules) but but instead break into smaller fragments known as microplastics. Microplastics have been detected in many ecosystems and in human tissues, and researchers are actively investigating their potential impacts on human health and the environment. One goal is to design plastics and other materials that can break down into less harmful substances at the end of their useful life, rather than persist in the environment. For example, chemists are investigating biodegradable polymers such as poly(lactic acid) (PLA) and poly(hydroxyalkanoates) (PHAs), which can be broken down under appropriate conditions into smaller molecules that can be processed by natural systems. These materials represent one possible approach to reducing the long-term environmental impacts associated with conventional plastics.

11. **Real-time analysis for Pollution Prevention**: *Analytical methodologies should be used to monitor chemical processes in real-time to*

provide efficient processes and prevent the formation of hazardous substances.

The goal of this principle is to detect and prevent the formation of hazardous substances before they are produced, rather than treating or disposing of waste afterward. Real-time monitoring tools, such as spectroscopic and sensor-based techniques, allow chemists to track reactions and optimize their conditions. By improving process control, this principle helps reduce waste, increase efficiency, enhance safety, and minimize environmental impact, making chemical manufacturing both more sustainable and economically advantageous.

12. **Inherently Safer Chemistry for Accident Prevention**: *Chemicals and processes should be chosen to minimize the potential for chemical accidents*

Green chemistry and safety go together. For a reaction to be considered "green", it should not use or produce hazardous substances (as described in GCP #3). However, not using or generating hazardous chemicals also makes these reactions safer to operate. As a result, if an accident occurs within a chemical factory, the consequences of the accident will be less damaging to the factory workers, the local community, and the environment. The best way to make something safer is to remove the possible hazards, instead of relying solely on procedures to manage toxic accidents.

You may have noticed that many of the Green Chemistry Principles overlap. This is intentional. Improving one aspect of a chemical process often leads to improvements in several others. For example, using a catalyst may reduce waste, improve atom economy, lower energy consumption, and eliminate the need for additional reaction steps. Green chemistry is therefore not a separate branch of chemistry, but rather a way of thinking about how we approach chemical problems. Chemists working in all areas of chemistry, from medicinal chemistry and materials science to analytical chemistry and biochemistry, can use the Green Chemistry Principles to guide the design of safer, more efficient, and more sustainable processes.

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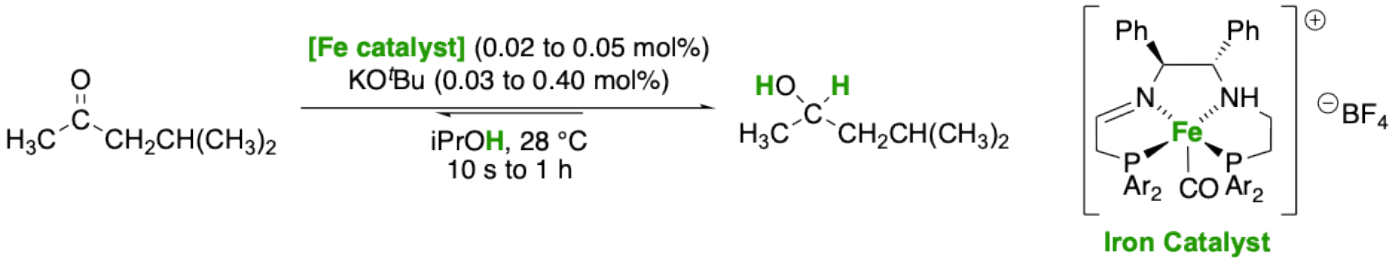
12.7.3: Green Chemistry and Sustainability at U of T

At the University of Toronto, we are applying green chemistry principles in our research. Meet some of the faculty whose research uses green chemistry principles.

undefined

Prof. Robert Morris is an inorganic chemistry professor who works on transition metal catalysis. A monumental contribution from the group was the development of an iron catalyst capable of reducing ketones with remarkable efficiency. Iron-based catalysts are particularly interesting because iron is cheap, abundant and less toxic, compared to its precious metal counterparts. Many precious metals are also endangered elements, meaning their supply is at risk due to high demand and limited availability. Not only was the Morris group able to make an iron catalyst capable of reducing ketones with remarkable activity comparable or even exceeding that of the precious metal catalysts (as little as 0.02 mol% catalyst needed and only as little as 10s to complete a reaction)!

As discussed in the previous section, chemists often address several Green Chemistry Principles (GPCs) when trying to make “greener” processes. For instance, this work used an iron catalyst instead of stochiometric reducing agents (GCP #9), which helped to minimize the amount of waste produced (GCP #1). The catalyst also allowed the reaction to be conducted under mild conditions (GCP #6) and possessed a high atom economy (GCP #2).



Check out the Morris research group here: https://sites.chem.utoronto.ca/chemistry/staff/rmorris/research_areas/research_areas.php

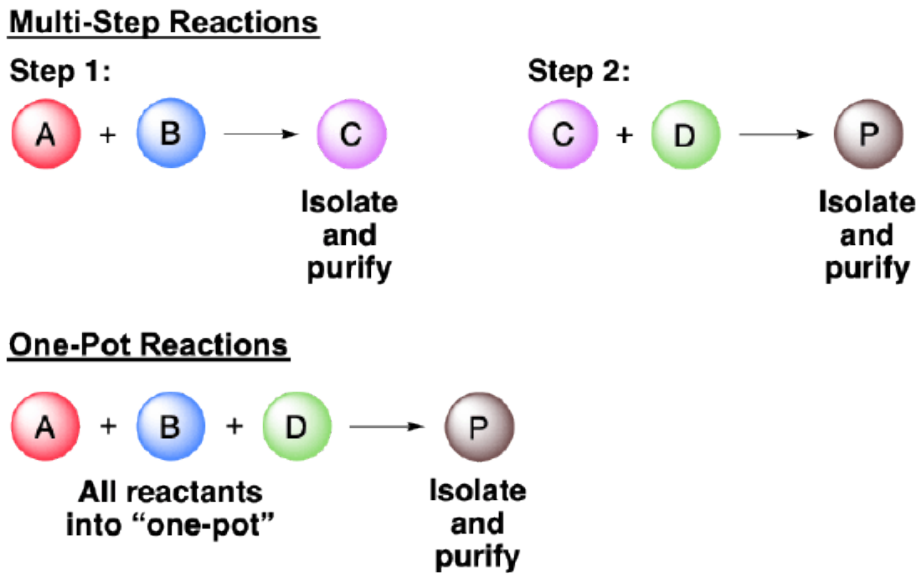
https://www.science.org/doi/abs/10.1126/science.1244466

https://www.acs.org/green-chemistry-sustainability/research-innovation/endangered-elements.html



Prof. Mark Lautens’ research group uses organic methodology and organometallic chemistry to improve the synthesis of organic molecules. One common strategy in the Lautens’ group is to combine a series of reactions into a single reaction vessel (also known as a “one-pot” reaction), which possesses several advantages in terms of the GCPs. For instance, this method reduces the number of derivatives (GCP #8) that need to be formed during a synthesis. As a result, the amount of waste is dramatically reduced (GCP #1) as intermediate compounds are

not being formed, isolated, purified, and then reacted in the next step. Isolation and purification steps are rarely shown in reaction equations but are almost always needed to produce a pure compound. These processes often require more materials than running the reaction itself and therefore produce the most chemical waste!



Check out the Lautens research group here: https://www.chem.utoronto.ca/ML/research.php



Prof. Helen Tran, a materials chemistry professor at U of T, works on developing biodegradable plastics (polymers) that support Green Chemistry Principle #10. These materials are designed to break down into harmless compounds rather than persist in the environment after they are used. The conventional plastics that we use daily do not breakdown in the environment. In 2023, the Tran group published work on a type of new polymers, poly(azomethine)s, that readily decompose into carotenoid in the presence of sunlight and/or acid-hydrolysis. Through optimization, the group developed a polymer that performs its intended function but can also be safely and efficiently broken down once it is no longer needed. Rather than persisting in landfills for years, the material can be degraded at the end of its useful life.

Check out the Tran research group: https://helen-t.com/research

https://pubs.rsc.org/en/content/articlepdf/2025/py/d5py00235d

https://pubs.acs.org/doi/pdf/10.1021/jacs.2c12668?ref=article_openPDF

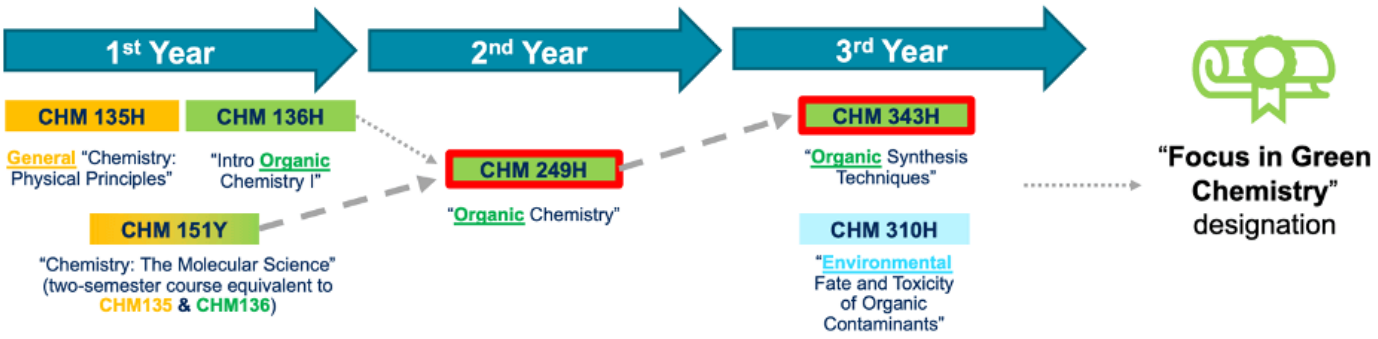


Another significant aspect that must be considered is the safety of the chemicals that we use and produce. Understanding chemical safety risk is directly related to GCP #4 − design for safer chemicals. If we can identify chemicals that are problematic, we can work to find appropriate replacements. This is where analytical and environmental chemists are instrumental, as they study how molecules behave in the environment and our bodies and the associated risks. Prof. Hui Peng's group studies the thousands of registered chemicals to understand how they interact with human proteins and to develop analytical methods to determine unknown contaminants in the environment.

Check out the Peng research group here: https://peng.chem.utoronto.ca/research

The examples above represent only a small snapshot of the wide range of green chemistry research being carried out in the Chemistry Department.

U of T's interest in green chemistry and sustainability is not limited to research applications like those highlighted above. The Department of Chemistry on the St. George campus has been incorporating green chemistry in their teaching practice for over two decades! Green chemistry is not a separate subdiscipline of chemistry; rather, it is a way of thinking that should guide all aspects of chemical research and practice. We believe that developing this mindset begins by encouraging the next generation of chemists to think about green and sustainable chemistry throughout their studies. If you are interested and passionate about green chemistry, consider taking the 'Focus in Green Chemistry' as a part of your studies here at U of T. For full details about this focus, check out the information at the following link: https://www.chemistry.utoronto.ca/programs-studies/focus-green-chemistry



Beyond the classrooms and the research laboratories, students at U of T are passionate about promoting green and sustainable chemistry. In 2012, the Green Chemistry Initiative (GCI) at U of T was founded and has continued to have a strong presence in the Department of Chemistry. The GCI is a student-led group with both graduate and undergraduate student members that work on different activities such as energy-reduction, trivia, seminar series and a symposium. The energy-reduction team serves to make sure we are using chemical equipment responsibly and not being wasteful with our energy and chemicals. This can range from checking that fumehoods are shut and promoting recycling of acetone, glassware and plastics used in the laboratory. Our trivia team makes green chemistry questions to encourage students to think about green solutions; if you answer the questions correctly, you can be entered for a chance to win a $10 gift card. Our seminar series and annual symposium provide opportunities to meet and connect with experts from academia and industry working in green chemistry. If these initiatives are interesting and you would like to get involved, consider joining as a 'member-at-large' where you support an executive

who is working on one of our many initiatives.

Check us out at: https://gci.chem.utoronto.ca/

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GLOSSARY

A

Absolute zero | 0 K or –273 °C; the lowest possible temperature

Absorption spectrum | spectrum produced by the emission of light by atoms as an electron moves from a lower energy level to a higher energy level

Acid ionization | reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

Acid ionization constant (K_a) | equilibrium constant for the ionization of a weak acid

Acid-base titration curve | plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

Acidic aqueous solution | solution for which water is the solvent and the concentration of hydronium ions ($[\mathrm{H_3O^+}]$) is greater than the concentration of hydroxide ions ($[\mathrm{OH^-}]$), resulting a pH value less than 7

Actinide | element of the set of transition metals located below the main table, with lanthanides

Activation energy (E_a) | energy necessary in order for a reaction to take place

Active electrode | electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

Actual yield | amount of product formed in a reaction

Alkali metal | element in group 1

Alkaline earth metal | element in group 2

Amphiprotic | species that may either gain or lose a proton in a reaction

Amplitude | extent of the displacement caused by a wave; for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude

Angular momentum quantum number (l) | quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

Anion | negatively charged atom or molecule (contains more electrons than protons)

Anode | electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

Arrhenius equation | mathematical relationship between the rate constant and the activation energy of a reaction

Atmosphere (atm) | unit of pressure; 1 atm = 101,325 Pa

Atmospheric pressure | the pressure exerted by the gases in Earth's atmosphere; approximately 101 kPa (1 atm) at sea level

Atom | smallest particle of an element that can enter into a chemical combination

Atomic mass | average mass of atoms of an element, expressed in amu

Atomic mass unit (amu) | unit of mass equal to 1/12 of the mass of a $^{12}\mathrm{C}$ atom; also called unified atomic mass unit (u) or Dalton (Da)

Atomic number (Z) | number of protons in the nucleus of an atom

Atomic orbital | region of space where an electron is most likely found, described by quantum numbers

Aufbau principle | dictates the procedure in which the electron configuration of the elements is determined by “building” them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

Autoionization | reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

Average kinetic energy (KE_{avg}) | The mean kinetic energy of particles in a gas; directly proportional to temperature

Average rate of reaction | rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

Avogadro's number (N_A) | experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} $\mathrm{mol^{-1}}$

Axial position | location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

B

Balanced chemical equation | chemical equation with equal numbers of atoms for each element in the reactant and product

Ball-and-stick model | 3D representation of molecules using spheres for atoms and sticks for bonds

Barometer | device used to measure atmospheric pressure in millimeters of mercury (mmHg) or torr

Base ionization | reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Base ionization constant (K_b) | equilibrium constant for the ionization of a weak base

Basic aqueous solution | solution for which water is the solvent and the concentration of hydroxide ions ($[\mathrm{OH^-}]$) is greater than the concentration of hydronium ions ($[\mathrm{H_3O^+}]$), resulting a pH value greater than 7

Bimolecular elementary reaction | reaction that involves the collision of two reactant particles

Binary acid | compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release $[\mathrm{H^+}]$ ions when dissolved in water)

Binary ionic compound | ionic compound containing two different elements, one metal and one nonmetal

Binding energy | the minimum energy required to remove an electron from an atom, result in an ion; also called ionization energy or threshold energy

Boiling point | temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Bomb calorimeter | device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

Bond angle | the angle between two bonds that share an atom, measured in degrees

Bond dipole moment | separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

Bond distance | distance between the nuclei of two bonded atoms, typically measured in Ångstroms or picometers; also called bond length

Bond energy | energy required to break a covalent bond in a gaseous substance; also called bond dissociation energy

Brønsted-Lowry acid | proton donor

Brønsted-Lowry base | proton acceptor

Buffer | mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Buffer capacity | amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

C

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

Calorimetry | process of measuring the amount of heat involved in a chemical or physical process

Catalyst | substance that increases the rate of a reaction without itself being consumed by the reaction

Cathode | electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

Cathodic protection | method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

Cation | positively charged atom or molecule (contains fewer electrons than protons)

Cell notation | shorthand way to represent the reactions in an electrochemical cell

Cell potential (E_{cell}) | difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions; also called electromotive force (EMF)

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

Chalcogen | element in group 16

Chemical activity (a) | unitless measure of concentration reflecting moderating effects such as attractions and repulsions between molecules

Chemical energy | the energy associated with the arrangement of atoms in a substance

Chemical equation | symbolic representation of a chemical reaction

Chemical 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

Chemical reaction | a process in which atoms are rearranged to form new substances with new properties

Chemical symbol | one-, two-, or three-letter abbreviation used to represent an element or its atoms

Chemistry | study of the composition, properties, and interactions of matter

Coefficient | number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

Collision theory | model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

Common ion effect | effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

Compound | pure substance that can be decomposed into two or more elements

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

Concentration cell | galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

Conjugate acid | substance formed when a base gains a proton

Conjugate base | substance formed when an acid loses a proton

Conjugate pair | pair of Brønsted-Lowry acid and its conjugate base or base and its conjugate acid

Constant-pressure calorimeter | calorimeter in which the pressure remains constant because the system is open to the atmosphere

Constant-volume calorimeter | calorimeter in which the volume remains constant, creating a closed system often used for non-gases

Constructive interference | occurs when the peaks of two electromagnetic waves align ("in phase") and their amplitudes add together, resulting in brighter light

Corrosion | degradation of metal through an electrochemical process

Covalent bonding | occurs when electrons are shared between atoms in a molecule or a polyatomic ion; most often occurs between nonmetals

Covalent compound | compound composed of molecules formed by atoms of two or more different elements

Covalent radius | one-half the distance between the nuclei of two identical bonded atoms

Critical point | temperature and pressure above which a gas cannot be condensed into a liquid

Current | flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes

D

***d* orbital** | region of space with high electron density that is either four-lobed or contains a dumbbell and torus shape; describes orbitals with l = 2; an electron in this orbital is called a d electron

Dalton's law of partial pressures | states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the individual gases

Density | ratio of mass to volume for a substance or object

Deposition | change from a gaseous state directly to a solid state

Derived SI unit | units derived from the seven SI base units

Destructive interference | occurs when the peak of one electromagnetic wave aligns with the trough of another ("out of phase") and their amplitudes cancel out, resulting in a smaller wave or no wave

Diffraction | redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

Diffusion | the movement of gas particles from an area of higher concentration to an area of lower concentration

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

Dipole moment | property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

Dipole-dipole attraction | intermolecular attraction between two permanent dipoles

Dispersion force | attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together; also called London dispersion force

Dissociation | physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and

dispersed throughout the solution

Dissolution | the process by which solute components are dispersed in a solvent

Double bond | covalent bond in which two pairs of electrons are shared between two atoms

Double slit experiment | investigation into the diffraction of light when waves pass through narrow slits, resulting in an interference pattern showing that light behaves as a wave

E

Effective nuclear charge (Z_{eff}) | charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

Effusion | the movement of gas particles through an opening smaller than the mean free path of the particles into an evacuated space

Electrical work ($w_{electric}$) | negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Electrochemistry | the study of the relationship between chemical reactions and electron flow

Electrolysis | process that uses electrical energy to drive a nonspontaneous redox reaction

Electrolytic cell | electrochemical cell with two electrodes in a single compartment where an external power source supplies electrical energy, generating a potential difference that forces electrons to flow and drives a nonspontaneous redox reaction

Electromagnetic radiation | energy transmitted by waves that have an electric-field component and a magnetic-field component

Electromagnetic spectrum | range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

Electron | negatively charged, subatomic particle of relatively low mass located outside the nucleus

Electron configuration | electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Electron density | a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

Electron shielding | occurs when inner electrons partially block the nuclear charge from outer electrons, reducing the effective nuclear charge (Z_{eff})

Electron-deficient molecule | molecule containing a central atom without a filled valence shell

Electronegativity | tendency of an atom to attract electrons in a bond to itself

Electroplating | coating objects with a thin metal layer via electrolysis

Electrostatic attraction | attraction between an atom's positively charged nucleus and the negatively charged electrons of another atom

Element | substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

Elementary reaction | step in a reaction mechanism that explicitly shows which particles collide, break apart, or rearrange to form the products and/or intermediates

Emission spectrum | spectrum produced by the emission of light by atoms as an electron moves from a higher energy level to a lower energy level

Empirical formula | formula showing the composition of a compound given as the simplest whole-number ratio of atoms

Endothermic | describes a chemical reaction or physical change that absorbs heat

Endpoint | measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see equivalence point)

Energy | capacity to supply heat or do work

Enthalpy (H) | sum of a system's internal energy and the mathematical product of its pressure and volume

Enthalpy change (ΔH) | heat released or absorbed by a system under constant pressure during a chemical or physical process

Entropy (S) | state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

Entropy change (ΔS) | increase or a decrease in the dispersal of energy in the system during a chemical or physical change

Enzyme | biological catalyst; usually large protein molecules with a small active site that binds the substrate and carries out the reaction

Equatorial position | one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

Equilibrium constant (*K*) | value of the reaction quotient for a system at equilibrium

Equivalence point | volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

Exact number | number derived by counting or by definition

Excess reactant | reactant present in an amount greater than required by the reaction stoichiometry

Excited state | state having an energy greater than the ground-state energy

Exothermic | describes a chemical reaction or physical change that releases heat

Expansion work (pressure-volume work) | type of mechanical work done as a system expands or contracts against external pressure

F

***f* orbital** | multi-lobed region of space with high electron density, describes orbitals with l = 3; an electron in this orbital is called an f electron

Faraday's constant (*F*) | charge on 1 mol of electrons; F = 96,485 C/mol e^-

First law of thermodynamics | internal energy of a system changes due to heat flow in or out of the system or work done on or by the system; also called the law of conservation of energy

Formula unit | the simplest ratio of ions in an ionic compound

Free radical | molecule that contains an odd number of electrons

Freezing | change from a liquid state to a solid state

Frequency (*ν*) | the number of wave cycles that pass a specified point in space in a specified amount of time; unit expressed as cycles per second (s^{-1}) or hertz (Hz)

Frequency factor (*A*) | proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

Fuel cell | galvanic cell that continuously converts chemical energy into electrical energy as long as fuel and an oxidant are supplied

G

Galvanic cell | electrochemical cell that turns chemical energy into electrical energy using spontaneous redox reactions; also called a voltaic cell

Gas | state in which matter has neither definite volume nor shape

Gibbs free energy (*G*) | thermodynamic property defined in terms of system enthalpy and entropy, allowing the prediction of spontaneity

Gibbs free energy change (Δ*G*) | the amount of energy available that can harnessed to do useful work in a thermodynamic system; equal to the sum of the enthalpy plus the product of the temperature and entropy of the system; can predict direction of chemical reaction under constant temperature and pressure

Ground state | state in which the electrons in an atom, ion, or molecule have the lowest energy possible

Group | vertical column of the periodic table

H

Half-life of a reaction ($t_{1/2}$) | time required for half of a given amount of reactant to be consumed

Half-reaction method | method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation "half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

Halogen | element in group 17

Heat (*q*) | transfer of thermal energy between two bodies

Heat capacity (*C*) | extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

Heating/cooling curve | graph illustrating how the temperature of a substance changes as it absorbs or releases heat

Heisenberg uncertainty principle | rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time; the uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

Henderson-Hasselbalch equation | equation used to calculate the pH of buffer solutions

Hertz (Hz) | the SI unit of frequency, which is the number of cycles per second, s^{-1}

Hess's law | rule stating that if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

Heterogeneous catalyst | catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

Heterogeneous equilibrium | equilibrium between reactants and products in different phases

Homogeneous catalyst | catalyst present in the same phase as the reactants

Homogeneous equilibrium | equilibrium within a single phase

Homogeneous mixture | combination of substances with a composition that is uniform throughout

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

Hydrogen bonding | occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

Hypervalent compound | molecule containing at least one main group element that has more than eight electrons in its valence shell

I

ICE table | method of calculating equilibrium concentration by tracking how a system moves from its initial concentration (I) through the changes (C) to equilibrium (E)

Ideal gas | hypothetical gas that behaves exactly as predicted by the ideal gas law

Ideal gas law | describes the behaviour of gases under many conditions; $PV = nRT$

Induced dipole | temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

Induced-fit model | model of enzyme function where the enzyme and substrate adjust their shapes upon binding to improve the fit

Inert electrode | electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive

Initial rate of reaction | instantaneous rate of a chemical reaction at t = 0 s (immediately after the reaction has begun)

Instantaneous rate of reaction | rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

Integrated rate law | equation that relates the concentration of a reactant to elapsed time of reaction

Interference pattern | pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

Intermolecular force | noncovalent attractive force between atoms, molecules, and/or ions

Internal energy (*E*) | total of all possible kinds of energy present in a substance or substances

Ion | electrically charged atom or molecule (contains unequal numbers of protons and electrons)

Ion product of water (K_w) | equilibrium constant for the autoionization reaction of water

Ion-dipole attraction | electrostatic attraction between an ion and a polar molecule

Ionic bonding | occurs when a metal donates one or more electrons to a nonmetal, forming oppositely charged ions

Ionic compound | compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

Ionic radius | measure of an ion's size, where cations are larger than the parent atom and anions are smaller

Ionic solid | solid composed of positive and negative ions held together by strong electrostatic attractions

Isoelectronic | describes a group of ions or atoms that have identical electron configurations

Isotope | atom that contains the same number of protons but different number of neutrons

J

Joule (J) | SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second; 1 J = 1 kg m^2/s and 4.184 J = 1 cal

K

K_c | equilibrium constant for reactions based on concentrations of reactants and products

Kelvin (K) | SI unit of temperature; 273.15 K = 0 °C

Kinetic energy | the energy of motion

Kinetic molecular theory | microscopic model explaining ideal gas behavior, postulating that gas particles move in straight lines unless interrupted by elastic collisions, particles are of negligible volume, particles' average kinetic energy is proportional to temperature, and gas pressure results from collisions with the container walls

K_p | equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

L

Lanthanide | element of the set of transition metals located below the main table, with actinides

Law of conservation of mass | states that atoms are neither created nor destroyed in a chemical reaction, but rather rearranged

Law of mass action | when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Le Chatelier's principle | when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

Lewis acid | substance that can accept a pair of electrons

Lewis base | substance that can donate a pair of electrons

Lewis structure | diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Limiting reactant | reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

Line spectrum | electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

Linear geometry | shape in which two outside groups are placed on opposite sides of a central atom

Liquid | state of matter that has a definite volume but indefinite shape

Lock-and-key model | model of enzyme function where the substrate fits precisely into the enzyme's active site

Lone pair | two (a pair of) valence electrons that are not used to form a bond

M

Macroscopic realm | everyday things that are large enough to sense directly by human sight and touch

Magnetic quantum number (m_l) | quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

Manometer | device used to measure the pressure of a gas trapped in a container, either relative to a vacuum (closed-end) or to atmospheric pressure (open-end)

Mass | fundamental property indicating amount of matter

Mass number (A) | sum of the numbers of neutrons and protons in the nucleus of an atom

Matter | anything that occupies space and has mass

Maxwell-Boltzmann distribution | function demonstrating the relative number of particles in a gas sample that move at a given speed

Mean free path | the average distance travelled between gas particle collisions

Melting | change from a solid state to a liquid state

Melting point | temperature at which the solid and liquid phases of a substance are in equilibrium

Metal | element that is shiny, malleable, good conductor of heat and electricity

Metallic bonding | occurs when valence electrons are delocalized across many atoms in a metal, forming a "sea of electrons" that allows metals to conduct electricity and be malleable

Metalloid | element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

Method of initial rates | use of a more explicit algebraic method to determine the orders in a rate law

Michaelis-Menten mechanism | describes how enzymes catalyze reactions through a two-step process; an enzyme binds a substrate to form an enzyme-substrate complex, which then breaks down to release the product while regenerating the enzyme

Microscopic realm | things that are much too small to be sensed directly

Microstate (*W*) | possible configuration or arrangement of matter and energy within a system

Midpoint | point on a titration curve halfway between start of the curve and the equivalence point, or between equivalence points in a polyprotic titration

Molar heat capacity (C_m) | amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; measured in J/(mol °C)

Molar mass | mass in grams of 1 mole of a substance

Molarity (M) | unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

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 $^{12}\mathrm{C}$

Mole ratio | unit conversation factor that relates the number of moles of substances in a balanced chemical equation

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

Molecular structure | structure that includes only the placement of the atoms in the molecule

Molecule | bonded collection of two or more atoms of the same or different elements

Monoprotic acid | acid containing one ionizable hydrogen atom per molecule

N

Nernst equation | equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

Neutral aqueous solution | solution for which water is the solvent and the concentration of hydronium ions ($[\mathrm{H_3O^+}]$) is equal to the concentration of hydroxide ions ($[\mathrm{OH^-}]$), resulting a pH value of 7

Neutralization reaction | reaction in which an acid and a base react to form a salt and water

Neutron | uncharged, subatomic particle located in the nucleus

Nobel Prize in Chemistry | prestigious international award recognizing groundbreaking contributions to the field of chemistry

Noble gas | element in group 18; also called inert gas

Node | any point of a standing wave with zero amplitude; also regions of an orbital where the probability of finding an electron is zero

Nonmetal | element that appears dull, poor conductor of heat and electricity

Nonspontaneous process | process that requires continual input of energy from an external source

Normal boiling point | temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

Nuclear energy | the energy stored in the nucleus of an atom, which can be released during nuclear reactions

Nucleus | massive, positively charged center of an atom made up of protons and neutrons

O

Octahedral geometry | shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated, with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

Octet rule | guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

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

Overall reaction order | sum of the reaction orders for each substance represented in the rate law

Overpotential | the extra voltage beyond the theoretical potential that is required to make a reaction occur at a practical rate

Oxidation | process in which a species loses electrons

Oxidation half-reaction | the "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

Oxidation number | tool to keep track of electron transfer during redox reactions, increasing upon oxidation and decreasing upon reduction; also called oxidation state

Oxidation-reduction reaction | broad type of reaction where one substance loses electrons through oxidation and another gains electrons through reduction; also called a redox reaction

Oxidizing agent | the species that accepts electrons from the other reactant and is itself reduced

Oxoacid | compound containing a nonmetal and one or more hydroxyl groups; also called oxyacid

P

***p* orbital** | dumbbell-shaped region of space with high electron density, describes orbitals with l = 1; an electron in this orbital is called a p electron

Parallel lines | lines in the same plane that do not intersect

Partial pressure | pressure exerted by an individual gas in a mixture of gases, independent of the pressures exerted by other gases

Pascal (Pa) | SI unit of pressure; 1 Pa = 1 N/m^2

Pauli exclusion principle | specifies that no two electrons in an atom can have the same value for all four quantum numbers

Penetration | the extent to which an electron in a subshell can approach the nucleus

Percent ionization | measure of acid or base strength; ratio of the concentration of the ionized acid/base to the initial acid/base concentration, multiplied by 100

Percent yield | measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

Period | horizontal row of the periodic table; also called a series

Perpendicular lines | lines in the same plane that form a right angle

pH | logarithmic measure of the concentration of hydronium ions in a solution

pH indicator | organic acid or base whose color changes depending on the pH of the solution it is in; permits visual detection of endpoint; also called acid-base indicator

Phase change | when a substance transitions between solid, liquid, and gas phases; also called phase transition

Phase diagram | pressure-temperature graph summarizing conditions under which the phases of a substance can exist

Photoelectric effect | the ejection of electrons from a metal's surface when irradiated by light above its threshold frequency

Photon | smallest possible packet of electromagnetic radiation, a particle of light

Pnictogen | element of group 15

pOH | logarithmic measure of the concentration of hydroxide ions in a solution

Polar covalent bond | covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

Polar molecule | molecule with an overall dipole moment

Polyatomic ion | ion composed of more than one atom

Polyprotic acid | acid with more than one ionizable proton per molecule, undergoing stepwise ionization

Polyprotic base | base that can accept more than one proton, undergoing stepwise protonation

Potential energy | stored energy due to position or arrangement

Precipitation | the process of dissolved ions in an aqueous solution reacting to form a solid precipitate

Pressure | force exerted per unit area

Principal quantum number (*n*) | quantum number specifying the shell an electron occupies in an atom

Product | substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

Proton | positively charged, subatomic particle located in the nucleus

Pure covalent bond | covalent bond between atoms of identical electronegativities; also called a nonpolar covalent bond

Q

Quantization | occurring only in specific discrete values, not continuous

Quantum mechanical model | Schrödinger's model of the atom treating electrons as three-dimensional waves spread out in a probability cloud (orbital) around the nucleus

R

Radial probability | the probability of finding an electron at a specific distance, r, from the nucleus

Radiant energy | the energy carried by electromagnetic waves

Rate constant (*k*) | proportionality constant in the relationship between reaction rate and concentrations of reactants

Rate determining step | the slowest step in the reaction mechanism; determines the overall reaction rate

Rate law | mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants;

also called rate equation

Reactant | substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

Reaction energy diagram | diagram that illustrates how energy changes during a reaction, including the transition states, activation energy barriers, and overall enthalpy change

Reaction intermediate | species with fully formed bonds that appears as a product in one step but is consumed in a subsequent step

Reaction mechanism | step-by-step series of simpler reactions by which an overall reaction takes place

Reaction order | value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

Reaction quotient (*Q*) | ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

Reaction rate | measure of the speed at which a chemical reaction takes place

Reducing agent | the species that provides electrons to the other reactant and is itself oxidized

Reduction | process in which a species gains electrons

Reduction half-reaction | the "half" of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

Reversible reaction | chemical reaction that can proceed in both the forward and reverse directions under given conditions

Root mean square velocity (u_{rms}) | the square root of the average of the squared velocities of particles in a gas

S

s orbital | spherical region of space with high electron density, describes orbitals with $l = 0$; an electron in this orbital is called an *s* electron

Salt bridge | galvanic cell component allowing ions to move between the half-cells to maintain electrical neutrality and preventing charge buildup

Salts | ionic compounds composed of cations and anions, either of which may react with water as acids or bases

Schrödinger equation | A mathematical framework developed by Erwin Schrödinger that describes the wave-like behavior of electrons; this equation can predict the energy levels of hydrogen, resulting in quantum numbers that define the properties of hydrogen orbitals

Scientific notation | a convenient method of expressing very large or very small numbers often used by scientists

Second law of thermodynamics | entropy of the universe increases for a spontaneous process

Shell | set of orbitals with the same principal quantum number, n

SI unit (International System of Units) | standards fixed by international agreement in the International System of Units (Le Système International d'Unités)

Significant figures | all of the measured digits in a determination, including the uncertain last digit; also called significant digits

Single bond | bond in which a single pair of electrons is shared between two atoms

Solid | state of matter that is rigid, has a definite shape, and has a fairly constant volume

Solubility equilibrium | equilibrium established when dissolution of a dissolving solid and precipitation of its ions happen at equal rates

Solubility product constant (K_{sp}) | equilibrium constant for a solid substance dissolving in an aqueous solution

Solute | solution component present in a concentration less than that of the solvent

Solution | a homogeneous mixture consisting of one or more solutes dissolved in a solvent

Solvent | solution component present in a concentration that is higher relative to other components

Space-filling model | 3D representation of molecules using spheres to show the relative size of atoms and how they fill space

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)

Speed | the distance a wave travels per unit time, measured in meters per second (m/s); the speed of a wave is equal to the product of its wavelength and frequency

Spin quantum number (m_s) | number specifying the electron spin direction, either +1/2 or -1/2

Spontaneous process | physical or chemical change that occurs without the addition of energy from an external source

Standard cell potential ($E°_{cell}$) | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 M for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

Standard enthalpies of formation ($\Delta H°_f$) | enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

Standard entropy change ($\Delta S°$) | change in entropy for a reaction calculated using the standard entropies, usually at room temperature

Standard free energies of formation ($\Delta G°_f$) | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

Standard free energy change ($\Delta G°$) | change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

Standard hydrogen electrode (SHE) | the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

Standard molar entropy ($S°$) | entropy of 1 mol of substance at a standard pressure of 1 atm

Standard molar volume | the volume one mole of an ideal gas occupies at STP, defined as 22.4 L

Standard oxidation potential ($E°_{ox}$) | measures how readily a substance loses electrons under standard conditions; the negative of the standard reduction potential for the reverse reaction

Standard reduction potential ($E°_{red}$) | measures how readily a species gains electrons under standard conditions (1 bar or 1 atm for gases; 1 M for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

Standard state conditions | set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Standard temperature and pressure (STP) | 273.15 K (0.00°C) and 1 atm; universal standard conditions used to compare gas properties

Standing wave | localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized; also called stationary wave

State function | property depending only on the state of a system, and not the path taken to reach that state

Stock solution | solution of a desired concentration diluted from a more concentrated one

Stoichiometry | the quantitative relationships between substances in a balanced chemical reaction

Strong acid | acidic substance that dissociates completely into ions in water

Strong base | basic substance that dissociates completely into ions in water

Structural formula | shows the atoms in a molecule and how they are connected

Sublimation | change from solid state directly to gaseous state

Subshell | set of orbitals in an atom with the same values of n and l

Substrate | reactant in an enzyme-catalyzed reaction

Supercritical fluid | substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

Surroundings | all matter other than the system being studied

Symbolic realm | specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

System | portion of matter undergoing a chemical or physical change being studied

T

Temperature | intensive property of matter that is a quantitative measure of “hotness” and “coldness”

Termolecular elementary reaction | rare reaction that involves three reactant particles colliding simultaneously

Tetrahedral geometry | shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

Theoretical yield | amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Thermal energy | kinetic energy associated with the random motion of atoms and molecules

Thermochemistry | study of measuring the amount of heat energy absorbed or released during a chemical reaction or a physical change

Thermodynamics | the study of energy and its transformations

Third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

Threshold frequency | frequency of light shone at a metal below which no electrons are ejected and above which the number of ejected electrons is proportional to light intensity

Torr | unit of pressure; 1 torr = 1/760 atm

Total pressure | the sum of the pressures that each gas in a mixture would exert if it were alone in the container

Transition metal | element in groups 3–11

Transition state | high-energy intermediate in which bonds are partially broken and formed

Trigonal bipyramidal geometry | shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

Trigonal planar geometry | shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

Triple bond | bond in which three pairs of electrons are shared between two atoms

Triple point | temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

U

Unimolecular elementary reaction | reaction that involves the rearrangement or decomposition of a single reactant molecule

Unit conversation factor | ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

V

Valence electron | electron in the outermost or valence shell (highest value of n) of a ground-state atom; determines how an element reacts

Valence Shell Electron-Shell 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

Vapor pressure | pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

Vaporization | change from liquid state to gaseous state

Voltage | a measure of the electrical potential difference between the two electrodes, indicating how much energy per unit charge can be obtained from a redox reaction

Voltmeter | instrument that measures electrical potential difference (voltage) between two electrodes in an electrochemical cell

Volume | amount of space occupied by an object

W

Wave | oscillation that can transport energy from one point to another in space

Wave-particle duality | term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Wavefunction (ψ) | mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

Wavelength (λ) | distance between two consecutive peaks or troughs in a wave

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

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Contributors

This online textbook was adapted from “Chemistry 2e” by OpenStax and substantially revised and adapted for students in CHM 135H at the University of Toronto. The majority of the development was carried out by Professor Kris Quinlan, with significant contributions from Professors Jessica D’eon, Aya Sakaya, and Kylie Luska.

The book has also been shaped by input from current and past CHM 135H students. Their feedback and experiences using the textbook have informed revisions to the content, organization, explanations, examples, and learning resources.

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