CHEM 108: TEXTBOOK



Greg Hershey Suryn
Gettysburg College



Chem 108: Textbook

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide an accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden born from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by NICE CXone Expert and was supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org or visit our main website at https://LibreTexts.org.

This text was compiled on 12/11/2025

TABLE OF CONTENTS

Licensing

12: Kinetics

- 12.1: Introduction
- 12.2: Summary
- 12.3: Exercises
- 12.4: Chemical Reaction Rates
- 12.5: Factors Affecting Reaction Rates
- 12.6: Rate Laws
- 12.7: Integrated Rate Laws
- 12.8: Collision Theory
- 12.9: Reaction Mechanisms
- 12.10: Catalysis
- 12.11: Key Terms
- 12.12: Key Equations

13: Fundamental Equilibrium Concepts

- 13.1: Introduction
- 13.2: Chemical Equilibria
- 13.3: Equilibrium Constants
- 13.4: Shifting Equilibria - Le Chatelier's Principle
- 13.5: Equilibrium Calculations
- 13.6: Key Terms
- 13.7: Key Equations
- 13.8: Summary
- 13.9: Exercises

14: Acid-Base Equilibria

- 14.1: Introduction
- 14.2: Summary
- 14.3: Exercises
- 14.4: Brønsted-Lowry Acids and Bases
- 14.5: pH and pOH
- 14.6: Relative Strengths of Acids and Bases
- 14.7: Hydrolysis of Salt Solutions
- 14.8: Polyprotic Acids
- 14.9: Buffers
- 14.10: Acid-Base Titrations
- 14.11: Key Terms
- 14.12: Key Equations

15: Equilibria of Other Reaction Classes

- 15.1: Introduction
- 15.2: Precipitation and Dissolution

- 15.3: Lewis Acids and Bases
- 15.4: Coupled Equilibria
- 15.5: Key Terms
- 15.6: Key Equations
- 15.7: Summary
- 15.8: Exercises

16: Thermochemistry

- 16.1: Introduction
- 16.2: Energy Basics
- 16.3: Calorimetry
- 16.4: Enthalpy
- 16.5: Key Terms
- 16.6: Key Equations
- 16.7: Summary
- 16.8: Exercises

17: Thermodynamics

- 17.1: Introduction
- 17.2: Spontaneity
- 17.3: Entropy
- 17.4: The Second and Third Laws of Thermodynamics
- 17.5: Free Energy
- 17.6: Key Terms
- 17.7: Key Equations
- 17.8: Summary
- 17.9: Exercises

18: Electrochemistry

- 18.1: Introduction
- 18.2: Summary
- 18.3: Exercises
- 18.4: Review of Redox Chemistry
- 18.5: Galvanic Cells
- 18.6: Electrode and Cell Potentials
- 18.7: Potential, Free Energy, and Equilibrium
- 18.8: Batteries and Fuel Cells
- 18.9: Corrosion
- 18.10: Electrolysis
- 18.11: Key Terms
- 18.12: Key Equations

19: Nuclear Chemistry

- 19.1: Introduction
- 19.2: Exercises
- 19.3: Nuclear Structure and Stability
- 19.4: Nuclear Equations
- 19.5: Radioactive Decay

- 19.6: Transmutation and Nuclear Energy
- 19.7: Uses of Radioisotopes
- 19.8: Biological Effects of Radiation
- 19.9: Key Terms
- 19.10: Key Equations
- 19.11: Summary

Index

Glossary

Detailed Licensing

Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

12: Kinetics

Chemical kinetics is the study of rates of chemical processes and includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

12.1: Introduction
12.2: Summary
12.3: Exercises
12.4: Chemical Reaction Rates
12.5: Factors Affecting Reaction Rates
12.6: Rate Laws
12.7: Integrated Rate Laws
12.8: Collision Theory
12.9: Reaction Mechanisms
12.10: Catalysis
12.11: Key Terms
12.12: Key Equations

This page titled 12: Kinetics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

12.1: Introduction

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. A cold lizard is a slower lizard and an easier meal for predators.



Figure **12.1.1**: An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. Two questions are typically posed when planning to carry out a chemical reaction. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. This chapter examines the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to describe the rates at which reactions occur.

This page titled 12.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.0: Introduction** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.2: Summary

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway with a lower activation energy.

Rate laws (*differential rate laws*) provide a mathematical description of how changes in the concentration of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the concentration of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Integrated rate laws are mathematically derived from differential rate laws, and they describe the time dependence of reactant and product concentrations.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. A reaction's half-life varies with rate constant and, for some reaction orders, reactant concentration. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

Chemical reactions typically require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant, activation energy, temperature, and dependence on collision orientation.

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The molecularity of an elementary reaction is the number of reactant species involved, typically one (unimolecular), two (bimolecular), or, less commonly, three (termolecular). The overall rate of a reaction is determined by the rate of the slowest in its mechanism, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

12.2: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **12.10: Summary** is licensed CC BY 4.0.

12.3: Exercises

1.

What is the difference between average rate, initial rate, and instantaneous rate?

2.

Ozone decomposes to oxygen according to the equation Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

3.

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

4.

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

Time (s)	0	1600	3200	4800	6200
$[C_4H_6]$ (M)	$1.00\ 10^{-2}$	$5.04\ 10^{-3}$	$3.37\ 10^{-3}$	$2.53\ 10^{-3}$	$2.08\ 10^{-3}$

a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?
c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

5.

A study of the rate of the reaction represented as gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.775	0.625	0.465	0.360	0.285	0.230

a. Determine the average rate of disappearance of A between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
b. Estimate the instantaneous rate of disappearance of A at 15.0 s from a graph of time versus [A]. What are the units of this rate?
c. Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.

6.

Consider the following reaction in aqueous solution:

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is $3.5\ 10^{-4}$ mol L^{-1} s^{-1}, what is the rate of appearance of $Br_2(aq)$ at that moment?

7.

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

8.

Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

9.

Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red

plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

a. What happens when the angle of the collision is changed?
b. Explain how this is relevant to rate of reaction.

10.

In the PhET Reactions & Rates interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

11.

In the PhET Reactions & Rates interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

a. Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?
b. Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

12.

How do the rate of a reaction and its rate constant differ?

13.

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

14.

Tripling the concentration of a reactant increases the rate of a reaction nine-fold. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four-fold. What is the order of the reaction with respect to that reactant?

15.

How will the rate of reaction change for the process: if the rate law for the reaction is

a. Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
b. Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

16.

How will each of the following affect the rate of the reaction: if the rate law for the reaction is ?

a. Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
b. Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

17.

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 depletion of the ozone layer. The reaction is first order with respect to both NO and O_3 with a rate constant of $2.20\ 10^7$ L/mol/s. What is the instantaneous rate of disappearance of NO when $[NO] = 3.3\ 10^{-6}$ *M* and $[O_3] = 5.9\ 10^{-7}$ *M*?

18.

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

rate = $4.85\ 10^{-2}$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

19.

The rate constant for the radioactive decay of ^{14}C is $1.21\ 10^{-4}$ $year^{-1}$. The products of the decay are nitrogen atoms and electrons (beta particles):

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of $6.5\ 10^{-9}$ *M*?

20.

The decomposition of acetaldehyde is a second order reaction with a rate constant of $4.71\ 10^{-8}$ L mol^{-1} s^{-1}. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of $5.55\ 10^{-4}$ *M*?

21.

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

$[C_2H_5OH]$ (*M*)	$4.4\ 10^{-2}$	$3.3\ 10^{-2}$	$2.2\ 10^{-2}$
Rate (mol L^{-1} h^{-1})	$2.0\ 10^{-2}$	$2.0\ 10^{-2}$	$2.0\ 10^{-2}$

Determine the rate law, the rate constant, and the overall order for this reaction.

22.

Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

$[NH_3]$ (*M*)	$1.0\ 10^{-3}$	$2.0\ 10^{-3}$	$3.0\ 10^{-3}$
Rate (mol L^{-1} h^{-1})	$1.5\ 10^{-6}$	$1.5\ 10^{-6}$	$1.5\ 10^{-6}$

Determine the rate law, the rate constant, and the overall order for this reaction.

23.

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (*M*)	0.10	0.20	0.30
Rate (mol L^{-1} h^{-1})	$8.0\ 10^{-10}$	$3.2\ 10^{-9}$	$7.2\ 10^{-9}$

24.

From the following data, determine the rate law, the rate constant, and the order with respect to *A* for the reaction

[*A*] (*M*)	$1.33\ 10^{-2}$	$2.66\ 10^{-2}$	$3.99\ 10^{-2}$
Rate (mol L^{-1} h^{-1})	$3.80\ 10^{-7}$	$1.52\ 10^{-6}$	$3.42\ 10^{-6}$

25.

Nitrogen monoxide reacts with chlorine according to the equation:

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L)	$[Cl_2]$ (mol/L)	Rate (mol L^{-1} h^{-1})
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

26.

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

Determine the rate law, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
$[H_2]$ (*M*)	0.35	0.35	0.70
Rate (mol L^{-1} s^{-1})	$2.835\ 10^{-3}$	$1.134\ 10^{-2}$	$2.268\ 10^{-2}$

27.

For the reaction the following data were obtained at 30 °C:

[*A*] (*M*)	0.230	0.356	0.557
Rate (mol L^{-1} s^{-1})	$4.17\ 10^{-4}$	$9.99\ 10^{-4}$	$2.44\ 10^{-3}$

a. What is the order of the reaction with respect to [*A*], and what is the rate law?
b. What is the rate constant?

28.

For the reaction the following data were obtained at 30 °C:

$[Q]_{initial}$ (*M*)	0.170	0.212	0.357
Rate (mol L^{-1} s^{-1})	$6.68\ 10^{-3}$	$1.04\ 10^{-2}$	$2.94\ 10^{-2}$

a. What is the order of the reaction with respect to [*Q*], and what is the rate law?
b. What is the rate constant?

29.

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is $6.2\ 10^{-4}$ min^{-1}.

What is the rate of the reaction when $[N_2O_5]$ = 0.40 *M*?

30.

The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

a. The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order

in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8 10^{-6} L^2 mol^{-2} s^{-1}.

31.

The following data have been determined for the reaction:

	1	2	3
(*M*)	0.10	0.20	0.30
(*M*)	0.050	0.050	0.010
Rate (mol L^{-1} s^{-1})	3.05 10^{-4}	6.20 10^{-4}	1.83 10^{-4}

Determine the rate law and the rate constant for this reaction.

32.

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of *A* at varying times.

33.

Use the data provided to graphically determine the order and rate constant of the following reaction:

Time (s)	0	5.00 10^3	1.00 10^4	1.50 10^4
[SO_2Cl_2] (*M*)	0.100	0.0896	0.0802	0.0719
Time (s)	2.50 10^4	3.00 10^4	4.00 10^4	
[SO_2Cl_2] (*M*)	0.0577	0.0517	0.0415	

34.

Pure ozone decomposes slowly to oxygen, Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	2.0 10^3	7.6 10^3	1.00 10^4
[O_3] (*M*)	1.00 10^{-5}	4.98 10^{-6}	2.07 10^{-6}	1.66 10^{-6}
Time (h)	1.23 10^4	1.43 10^4	1.70 10^4	
[O_3] (*M*)	1.39 10^{-6}	1.22 10^{-6}	1.05 10^{-6}	

35.

From the given data, use a graphical method to determine the order and rate constant of the following reaction:

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[*X*] (*M*)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

36.

What is the half-life for the first-order decay of phosphorus-32? The rate constant for the decay is 4.85 10^{-2} day^{-1}.

37.

What is the half-life for the first-order decay of carbon-14? The rate constant for the decay is 1.21 10^{-4} $year^{-1}$.

38.

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0 10^{-8} L mol^{-1} s^{-1}.

39.

What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35 10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L mol^{-1} h^{-1}.

40.

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 L mol^{-1} s^{-1}. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

41.

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 min when the initial concentration of *A* is 0.150 M. How long will it take for the concentration to drop to 0.0300 M if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

42.

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3 10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate law that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15 10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

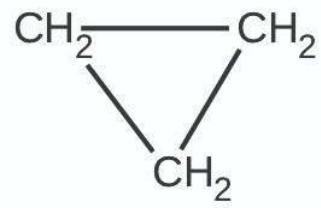
[Penicillin] (*M*)	Rate (mol L^{-1} min^{-1})
2.0 10^{-6}	1.0 10^{-10}
3.0 10^{-6}	1.5 10^{-10}
4.0 10^{-6}	2.0 10^{-10}

43.

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

44.

There are two molecules with the formula C_3H_6. Propene, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of 5.95 10^{-4} s^{-1}. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

45.

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the equation is Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

a. What is the rate constant for the decomposition of fluorine-18?

b. If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?

c. How long does it take for 99.99% of the ^{18}F to decay?

46.

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 of the initial dose to remain in the athlete's body?

47.

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

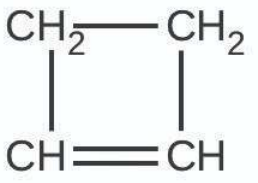
48.

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

49.

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order 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.

50.

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

51.

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

52.

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

53.

Account for the relationship between the rate of a reaction and its activation energy.

54.

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

55.

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

56.

The rate of a certain reaction doubles for every 10 °C rise in temperature.

a. How much faster does the reaction proceed at 45 °C than at 25 °C?
b. How much faster does the reaction proceed at 95 °C than at 25 °C?

57.

In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)

58.

The rate constant at 325 °C for the decomposition reaction is 6.1 10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

59.

The rate constant for the decomposition of acetaldehyde, CH_3CHO, to methane, CH_4, and carbon monoxide, CO, in the gas phase is 1.1 10^{-2} L mol^{-1} s^{-1} at 703 K and 4.95 L mol^{-1} s^{-1} at 865 K. Determine the activation energy for this decomposition.

60.

An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. 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?

61.

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

a. the change in free energy per second
b. the change in temperature per second
c. the number of collisions per second
d. the number of product molecules

62.

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, *k*, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	*k* (L mol^{-1} s^{-1})
555	6.23 10^{-7}
575	2.42 10^{-6}
645	1.44 10^{-4}
700	2.01 10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

63.

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})
293	0.054
298	0.100

64.

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

follows a first-order rate law for the disappearance of sucrose: rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

a. In neutral solution, $k = 2.1\ 10^{-11}\ s^{-1}$ at 27 °C and $8.5\ 10^{-11}\ s^{-1}$ at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).
b. When a solution of sucrose with an initial concentration of 0.150 *M* reaches equilibrium, the concentration of sucrose is $1.65\ 10^{-7}$ *M*. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.
c. Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

65.

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

66.

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

67.

Why are elementary reactions involving three or more reactants very uncommon?

68.

In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction ? Can we predict the effect if the reaction is known to be an elementary reaction?

69.

Define these terms:

a. unimolecular reaction
b. bimolecular reaction
c. elementary reaction
d. overall reaction

70.

What is the rate law for the elementary termolecular reaction For

71.

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

72.

Write the rate law for each of the following elementary reactions:

a.
b.
c.
d.
e.

73.

Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:

What would the rate law be if the mechanism for this reaction were:

74.

Experiments were conducted to study the rate of the reaction represented by this equation.[2]

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol L^{-1})	Initial Concentration, [H_2] (mol L^{-1} min^{-1})	Initial Rate of Formation of N_2 (mol L^{-1} min^{-1})
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. Step 3:

75.

The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:
(fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
(slow, k_2 the rate constant)
(fast, k_3 the rate constant)

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.

76.

Account for the increase in reaction rate brought about by a catalyst.

77.

Compare the functions of homogeneous and heterogeneous catalysts.

78.

Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:

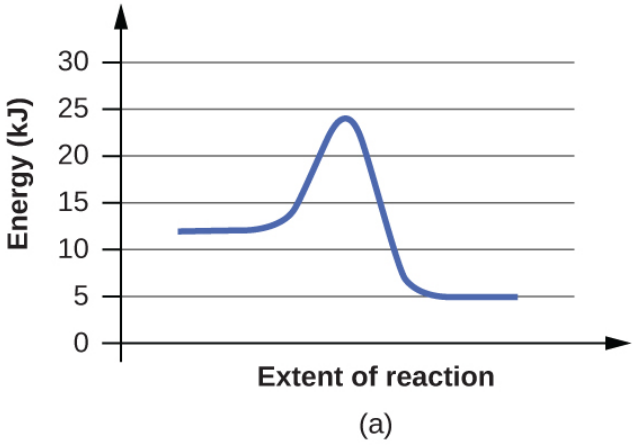
(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

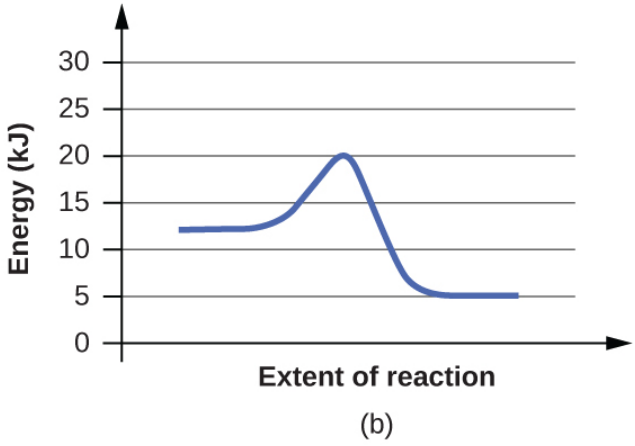
Is NO a catalyst for the decomposition? Explain your answer.

79.

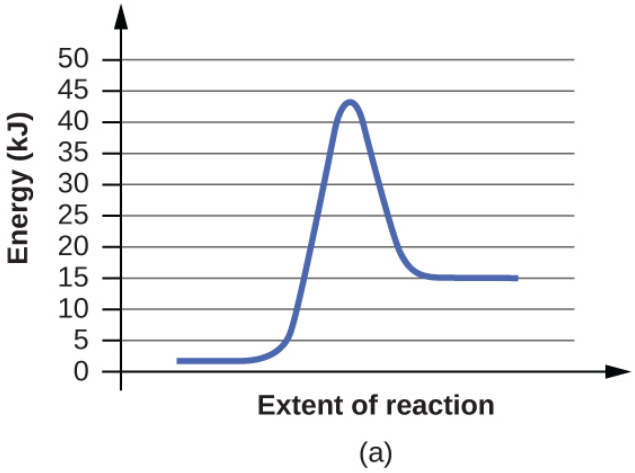
For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

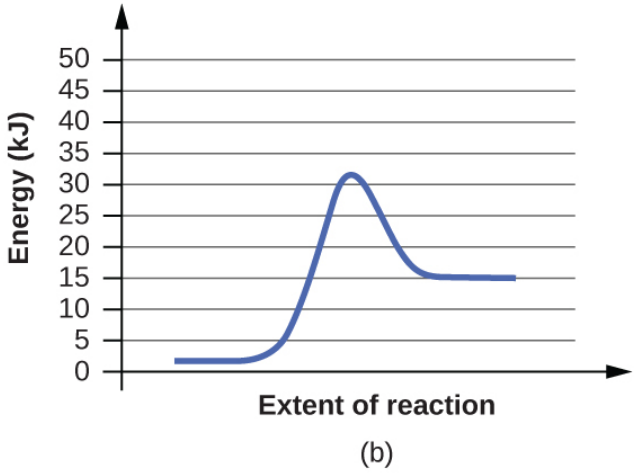
(a)





(b)



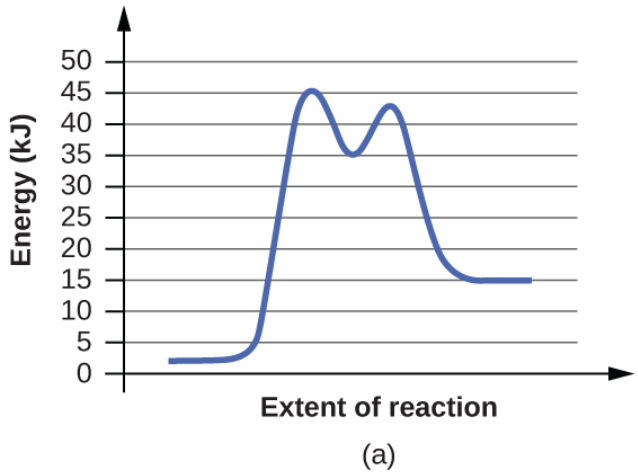


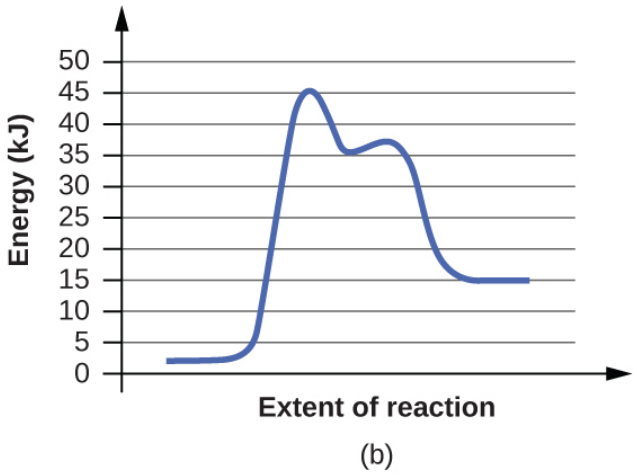
80.

For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

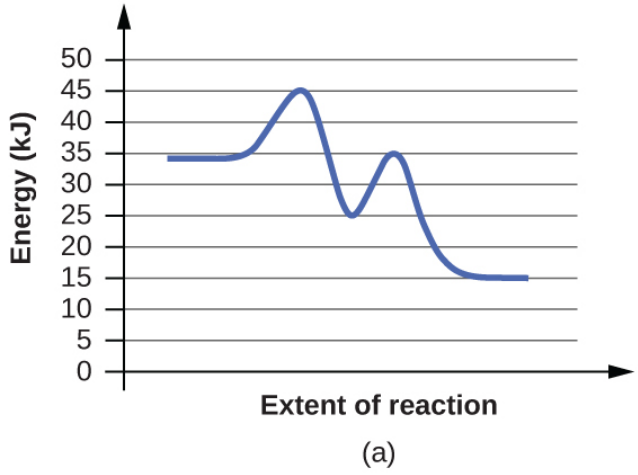
(a)

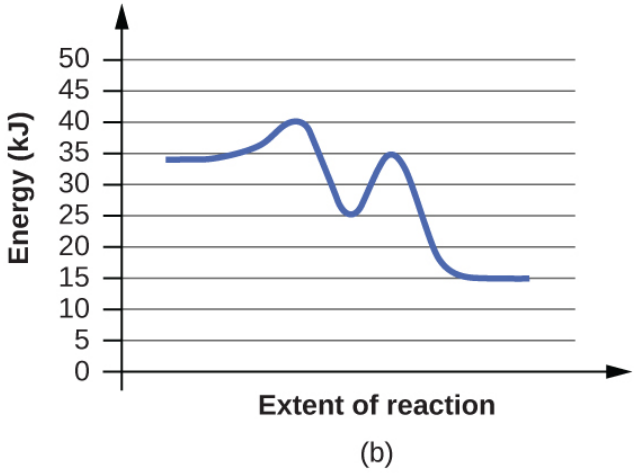
https://chem.libretexts.org/@go/page/548563





(b)

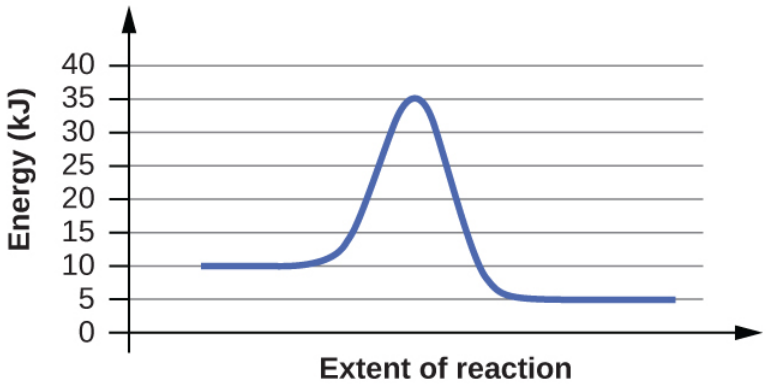




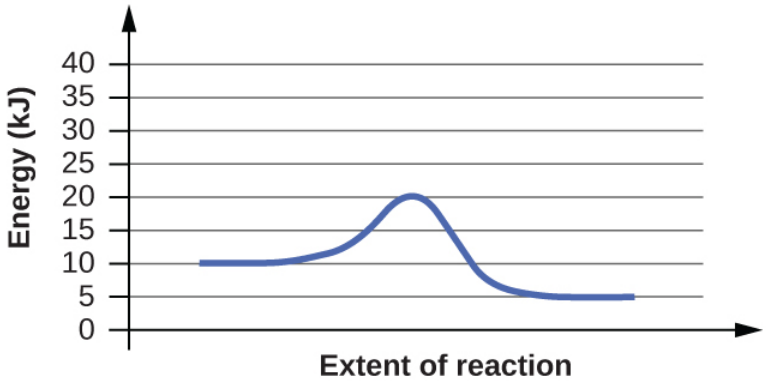
81.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



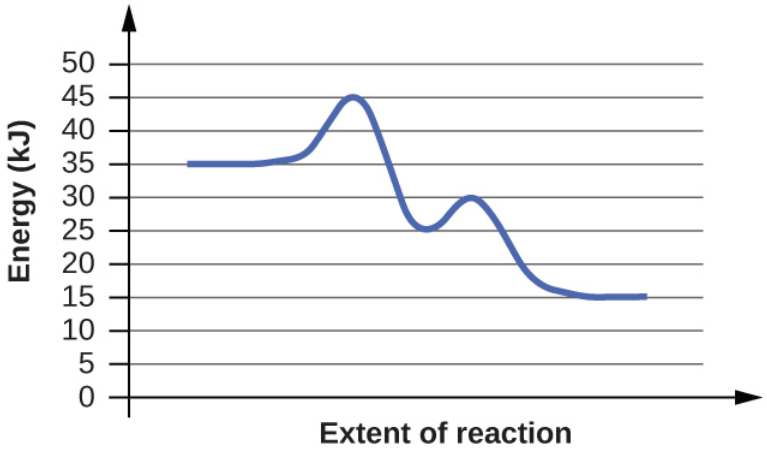
(b)



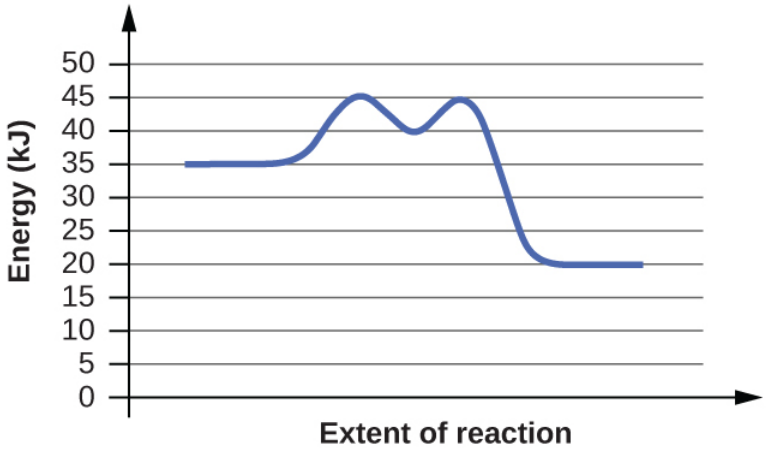
82.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



83.

Assuming the diagrams in Exercise 12.81 represent different mechanisms for the same reaction, which of the reactions has the faster rate?

84.

Consider the similarities and differences in the two reaction diagrams shown in Exercise 12.82. Do these diagrams represent two different overall reactions, or do they represent the same overall reaction taking place by two different mechanisms? Explain your answer.

Footnotes

- 2This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

This page titled 12.3: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.11: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.4: Chemical Reaction Rates

Learning Objectives

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

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

Erroneous nesting of equation structures

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\mathbf{H_2O_2}]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[\mathbf{H_2O_2}]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t2; and Δ[H2O2] represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[\mathbf{H_2O_2}]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. Figure **12.4.1** provides an example of data collected during the decomposition of $\mathbf{H_2O_2}$.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
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	0.010
24.00	0.0625			

Figure **12.4.1**: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.500 mol/L - 1.000 mol/L)}{(6.00 h - 0.00 h)} = 0.0833 mol L^{-1} h^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.0625 mol/L - 0.125 mol/L)}{(24.00 h - 18.00 h)} = 0.010 mol L^{-1} h^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. In a plot of the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of $\mathbf{H_2O_2}$ at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure **12.4.2**). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

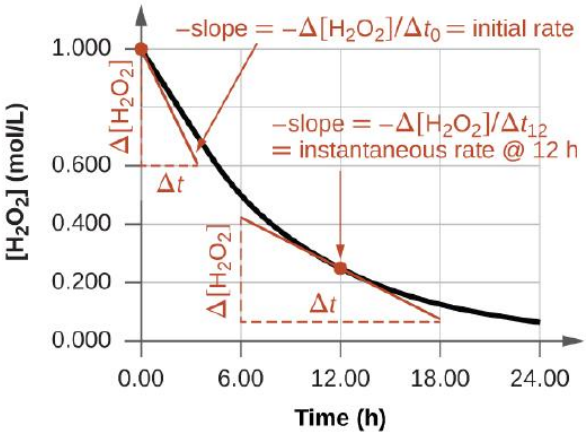


Figure **12.4.2**: This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at 12 h).

Chemistry in Everyday Life: 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 **12.4.3**). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

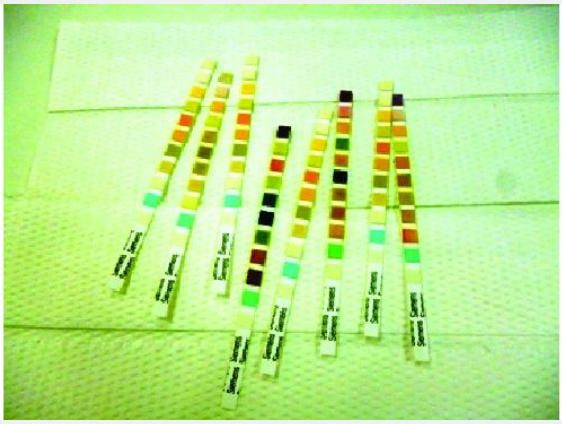


Figure **12.4.3**: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$A \longrightarrow B \tag{12.4.1}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate} = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

Consider the reaction represented by the following equation:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta mol\ NH_3}{\Delta t} \times \frac{1 mol\ N_2}{2 mol\ NH_3} = \frac{\Delta mol\ N_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta mol\ NH_3}{\Delta t} = \frac{\Delta mol\ N_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are

present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

Figure 12.4.4: illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at t = 500 s show that the instantaneous rates derived from all three species involved in the reaction are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6} M/s}{9.70 \times 10^{-7} M/s} \approx 3$$

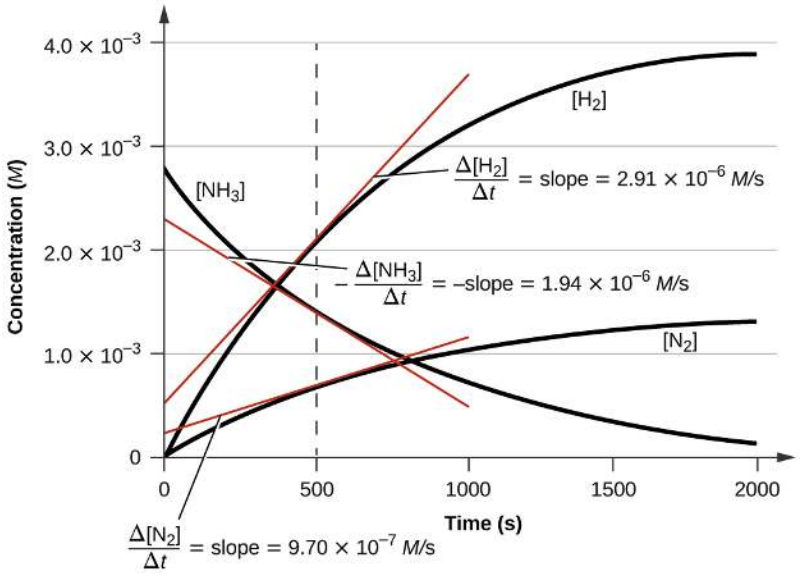


Figure 12.4.4: Changes in concentrations of the reactant and products for the reaction $2\,NH_3 \longrightarrow N_2 + 3\,H_2$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

Example 12.4.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \tag{12.4.2}$$

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 12.4.1

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:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

Example 12.4.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure **12.4.2**: shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20 10^{-2} mol/L/h, that is:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t} \tag{12.4.3}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t} \tag{12.4.4}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} molL^{-1}h^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2} molL^{-1}h^{-1}$$

Exercise 12.4.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10 10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer

1.05 10^{-6} mol/L/s, N_2 and 3.15 10^{-6} mol/L/s, H_2.

This page titled 12.4: Chemical Reaction Rates is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.1: Chemical Reaction Rates** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.5: Factors Affecting Reaction Rates

Learning Objectives

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

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 12.5.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure 12.5.1: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq)\ 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot

plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure **12.5.2**). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathrm{SO_2\,(g) + H_2O\,(g) \longrightarrow H_2SO_3\,(aq)}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathrm{CaCO_3\,(s) + H_2SO_3\,(aq) \longrightarrow CaSO_3\,(aq) + CO_2\,(g) + H_2O\,(l)}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



Figure **12.5.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Link to Learning

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, $\mathrm{H_2O_2}$, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$\mathrm{2\,H_2O_2\,(aq) \longrightarrow 2\,H_2O\,(l) + O_2\,(g)}$$

Under typical conditions, this decomposition occurs very slowly. When dilute $\mathrm{H_2O_2\,(aq)}$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

This page titled 12.5: Factors Affecting Reaction Rates is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.2: Factors Affecting Reaction Rates** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.6: Rate Laws

Learning Objectives

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

- 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

As described in the previous module, the rate of a reaction is often affected by the concentrations of reactants. Rate laws (sometimes called *differential rate laws*) or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow \text{ products}$$

where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate } = k[A]^m[B]^n$$

in which [*A*] and [*B*] represent the molar concentrations of reactants, and *k* is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents *m* and *n* are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant *k* and the reaction orders *m* and *n* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is *m* order with respect to *A* and *n* order with respect to *B*. For example, if *m* = 1 and *n* = 2, the reaction is first order in *A* and second order in *B*. The overall reaction order is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall (1 + 2 = 3). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate } = k\,[H_2O_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate } = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate } = k\,[\text{H}^+]\,[\text{OH}^-]$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Example 12.6.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2\,(\text{g}) + \text{CO}\,(\text{g}) \longrightarrow \text{NO}\,(\text{g}) + \text{CO}_2\,(\text{g})$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate } = k[\text{NO}_2]^m[\text{CO}]^n$$

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 $[\mathrm{CO}]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of $\mathrm{NO_2}$. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

? Exercise 12.6.1*A*

The rate law for the reaction:

$$\mathrm{H_2\,(g) + 2\,NO\,(g) \longrightarrow N_2O\,(g) + H_2O\,(g)}$$

has been determined to be 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

order in NO = 2; order in $\mathrm{H_2}$ = 1; overall order = 3

? Exercise 12.6.1*B*

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol ($\mathrm{CH_3OH}$) and ethyl acetate ($\mathrm{CH_3CH_2OCOCH_3}$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k\,[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

order in $\mathrm{CH_3OH}$ = 1; order in $\mathrm{CH_3CH_2OCOCH_3}$ = 0; overall order = 1

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

✓ Example 12.6.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure **12.6.1**). One such reaction is the combination of nitric oxide, NO, with ozone, $\mathrm{O_3}$:

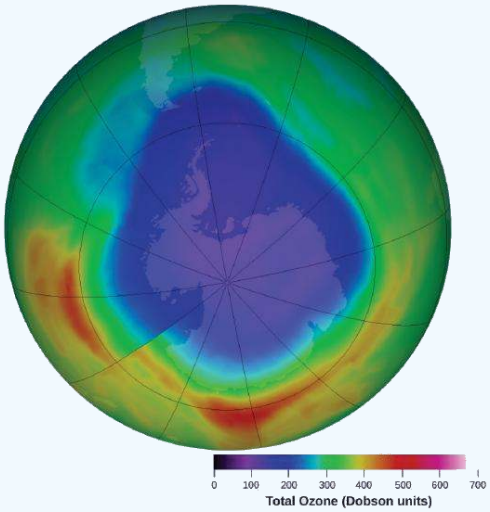


Figure **12.6.1**: A contour map showing stratospheric ozone concentration and the "ozone hole" that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

$$\mathbf{NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)}$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}\,(\mathrm{mol\,L^{-1}\,s^{-1}})$
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:

$$\mathbf{rate} = k[NO]^m[O_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

Step 1:

Determine the value of m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.

Step 2:

Determine the value of n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\mathbf{rate} = k[NO]^1[O_3]^1 = k[NO]\,[O_3]$$

Step 3:

Determine the value of k *from one set of concentrations and the corresponding rate*. The data from trial 1 are used below:

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}]\,[\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}}{(1.00 \times 10^{-6}\ \text{mol L}^{-1})\,(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\text{s}^{-1} \end{aligned}$$

? Exercise 12.6.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}\,(\text{g}) \longrightarrow \text{CH}_4\,(\text{g}) + \text{CO}\,(\text{g})$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH_3CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}\,(\text{mol L}^{-1}\text{s}^{-1})$
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

$\text{rate} = k[\text{CH}_3\text{CHO}]^2$ with k = 6.7310^{-6} L/mol/s

✓ Example 12.6.3: 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:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{CO}]}{\Delta t}\,(\text{mol } L^{-1}\text{s}^{-1})$
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:

$$\text{rate} = k[NO]^m[Cl_2]^n$$

As in Example **12.6.2**, approach this problem in a stepwise fashion, 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, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of *m* and *n*:

Step 1

Determine the value of m from the data in which [NO] varies and [Cl_2] is constant. Write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[NO]_x^m[Cl_2]_x^n}{k[NO]_y^m[Cl_2]_y^n}$$

Using the third trial and the first trial, in which $[Cl_2]$ does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

Use logarithms to determine the value of the exponent m:

$$\ln(2.25) = m\ln(1.5)$$

$$\frac{\ln(2.25)}{\ln(1.5)} = m$$

$$2 = m$$

Confirm the result

$$1.5^2 = 2.25$$

Step 2

Determine the value of n from data in which $[Cl_2]$ varies and [NO] is constant.

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancelation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

which simplifies to:

$$1.5 = (1.5)^n$$

Thus n must be 1, and the form of the rate law is:

$$\text{rate } = k[NO]^m[Cl_2]^n = k[NO]^2\,[Cl_2]$$

Step 3.

Determine the numerical value of the constant with appropriate units. The units for the rate of a reaction are mol/L/s. The units for are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be mol^- L/s so that the rate is in terms of mol/L/s.

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*:

$$0.00300 \text{ mol L}^{-1}\text{s}^{-1} = k\left(0.10 \text{ mol L}^{-1}\right)^2\left(0.10 \text{ mol L}^{-1}\right)^1$$

$$k = 3.0 \text{ mol}^{-2}\text{L}^2\text{s}^{-1}$$

? Exercise 12.6.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$$

Trial	[OCl^-] (mol/L)	[I^-] (mol/L)	Initial Rate (mol/L/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

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate} = k[OCl^-]^2[I^-]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 mol^{-2}L^2s^{-1}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$\begin{aligned}
NO_2 + CO &\longrightarrow NO + CO_2 & \text{rate} &= k[NO_2]^2 \\
CH_3\,CHO &\longrightarrow CH_4 + CO & \text{rate} &= k[CH_3CHO]^2 \\
2\,N_2\,O_5 &\longrightarrow NO_2 + O_2 & \text{rate} &= k\,[N_2O_5] \\
2\,NO_2 + F_2 &\longrightarrow 2\,NO_2\,F & \text{rate} &= k\,[NO_2]\,[F_2] \\
2\,NO_2\,Cl &\longrightarrow 2\,NO_2 + Cl_2 & \text{rate} &= k\,[NO_2Cl]
\end{aligned}$$

Note

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in Example **12.6.2** was determined to be k was derived to be $\text{L mol}^{-1}\text{s}^{-1}$. For the third-order reaction, k was derived to be $\text{L}^2\text{mol}^{-2}\text{s}^{-1}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $\text{L}^{x-1}\,\text{mol}^{1-x}\text{s}^{-1}$. Table **12.6.1** summarizes the rate constant units for common reaction orders.

Table **12.6.1**: Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit ($L^{x-1}\ mol^{1-x}\ s^{-1}$)
0 (zero)	$mol\ L^{-1}\ s^{-1}$
1 (first)	s^{-1}
2 (second)	$L\ mol^{-1}\ s^{-1}$
3 (third)	$L^2\ mol^{-2}\ s^{-1}$

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

This page titled 12.6: Rate Laws is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.3: Rate Laws** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.7: Integrated Rate Laws

Learning Objectives

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

- 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 from concentration/time data

The rate laws discussed thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

or

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

and a format showing a linear dependence of concentration in time:

$$\ln [A]_t = \ln [A]_0 - kt$$

Example 12.7.1: 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 the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or 0.200x. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.7 \times 10^{2}\ \text{s} \end{aligned}$$

? Exercise 12.7.1

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}. How many days will it take for 90% of the iodine−131 in a 0.500 M solution of this substance to decay to Xe-131?

Answer

16.7 days

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\ln [A]_t = (-k)(t) + \ln [A]_0$$
$$y = mx + b$$

A plot of $\ln[A]_t$ versus t for a first-order reaction is a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A.

✓ Example 12.7.2: Graphical Determination of Reaction Order and Rate Constant

Show that the data in Figure **12.7.1** can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

Solution

The data from Figure **12.7.1** are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in Figure **12.7.1**.

Time (h)	$[H_2O_2]$ (M)	$\ln[H_2O_2]$
0.00	1.000	0.000
6.00	0.500	−0.693
12.00	0.250	−1.386
18.00	0.125	−2.079
24.00	0.0625	−2.772

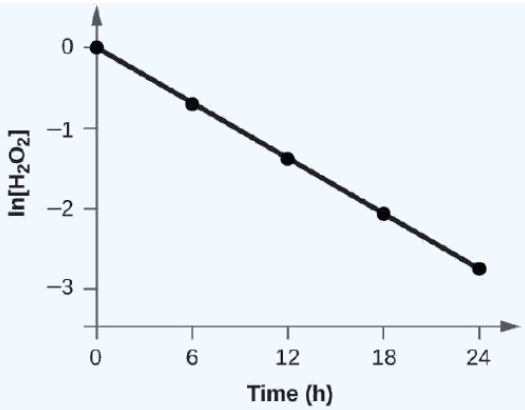


Figure **12.7.1**: A linear relationship between $\ln[H_2O_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

The plot of $\ln[H_2O_2]$ versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln [H_2O_2]}{\Delta t}$$

The slope of this line may be derived from 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 0.00 h is 0.000; the value when t = 24.00 h is −2.772

$$\begin{aligned} \text{slope} &= \frac{-2.772 - 0.000}{24.00 - 0.00h} \\ &= \frac{-2.772}{24.00h} \\ &= -0.116h^{-1} \\ k = -\text{ slope} &= -\left(-0.116h^{-1}\right) = 0.116h^{-1} \end{aligned}$$

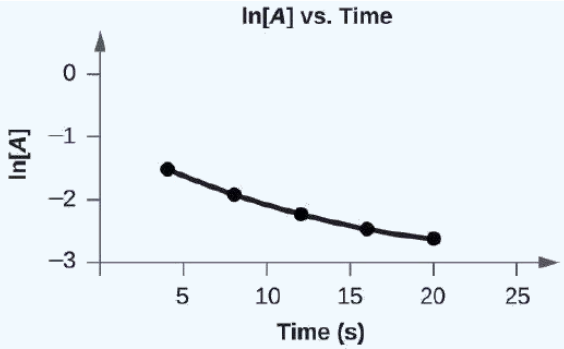
Exercise 12.7.2

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Time (s)	[A]
4.0	0.220
8.0	0.144
12.0	0.110
16.0	0.088
20.0	0.074

Answer

The plot of $\ln[A]_t$ vs. t is not linear, indicating the reaction is not first order:



Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

$$\text{rate} = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 12.7.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

This "dimerization" reaction is second order with a rate constant equal to 5.76 10^{-2} L mol^{-1} min^{-1} under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration after 10.0 min?

Solution

For a second-order reaction, the integrated rate law is written

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, k = 5.76 10^{-2} L/mol/min, and t = 10.0 min. Therefore, we can solve for [*A*], the fourth variable:

$$\begin{aligned}\frac{1}{[A]_t} &= \left(5.76 \times 10^{-2} L mol^{-1} min^{-1}\right)(10 min) + \frac{1}{0.200 mol^{-1}} \\ &= \left(5.76 \times 10^{-1} L mol^{-1}\right) + 5.00 L mol^{-1} \\ &= 5.58 L mol^{-1} \\ [A]_t &= 1.79 \times 10^{-1} mol L^{-1}\end{aligned}$$

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 12.7.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer

0.0195 mol/L

The integrated rate law for second-order reactions has the form of the equation of a straight line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$
$$y = mx + b$$

A plot of $\frac{1}{[A]_t}$ versus t for a second-order reaction is a straight line with a slope of k and a y-intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 12.7.4: Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example 12.7.3. Prepare and compare two appropriate data plots to identify the reaction as being either first or second order. After identifying the reaction order, estimate a value for the rate constant.

Solution

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}

In order to distinguish a first-order reaction from a second-order reaction, prepare a plot of $\ln[C_4H_6]_t$ versus t and compare it to a plot of $\frac{1}{[C_4H_6]_t}$ 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
6200	481	−6.175

The plots are shown in Figure 12.7.2, which clearly shows the plot of $\ln[C_4H_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]_t}$ versus t is linear, indicating that the reaction is second order.

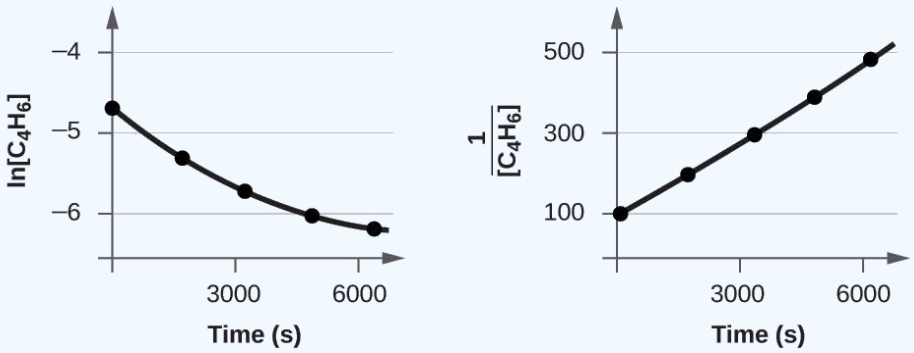


Figure 12.7.2: These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

According to the second-order integrated rate law, the rate constant is equal to the slope of the versus t plot. Using the data for t = 0 s and t = 6200 s, the rate constant is estimated as follows:

$$k = \text{ slope } = \frac{(481M^{-1} - 100M^{-1})}{(6200s - 0s)} = 0.0614M^{-1}s^{-1}$$

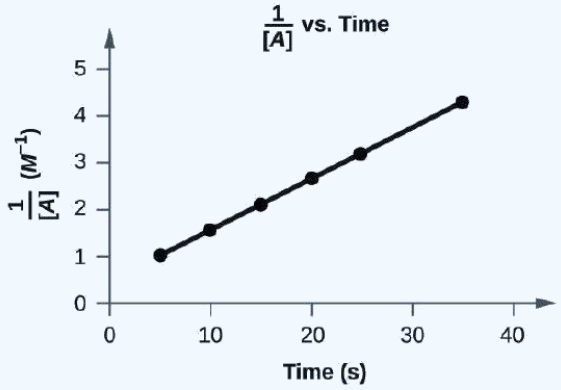
? Exercise 12.7.4

Do the following data fit a second-order rate law?

Time (s)	[A] (M)
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

Answer

Yes. The plot of $\frac{1}{[A]_t}$ vs. t is linear:



Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{rate } = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s). This may seem counterintuitive, since the reaction rate certainly can't be finite when the reactant concentration is zero. For purposes of this introductory text, it will suffice to note that zero-order kinetics are observed for some reactions only under certain specific conditions. These same reactions exhibit different kinetic behaviors when the specific conditions aren't met, and for this reason the more prudent term *pseudo-zero-order* is sometimes used.

The integrated rate law for a zero-order reaction is a linear function:

$$[A]_t = -kt + [A]_0$$
$$y = mx + b$$

A plot of [A] versus t for a zero-order reaction is a straight line with a slope of $-k$ and a y-intercept of $[A]_0$. Figure **12.7.3**: shows a plot of [NH_3] versus t for the thermal decomposition of ammonia at the surface of two different heated solids. The decomposition

reaction exhibits first-order behavior at a quartz (SiO_2) surface, as suggested by the exponentially decaying plot of concentration versus time. On a tungsten surface, however, the plot is linear, indicating zero-order kinetics.

Example 12.7.5: Graphical Determination of Zero-Order Rate Constant

Use the data plot in Figure **12.7.3** to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

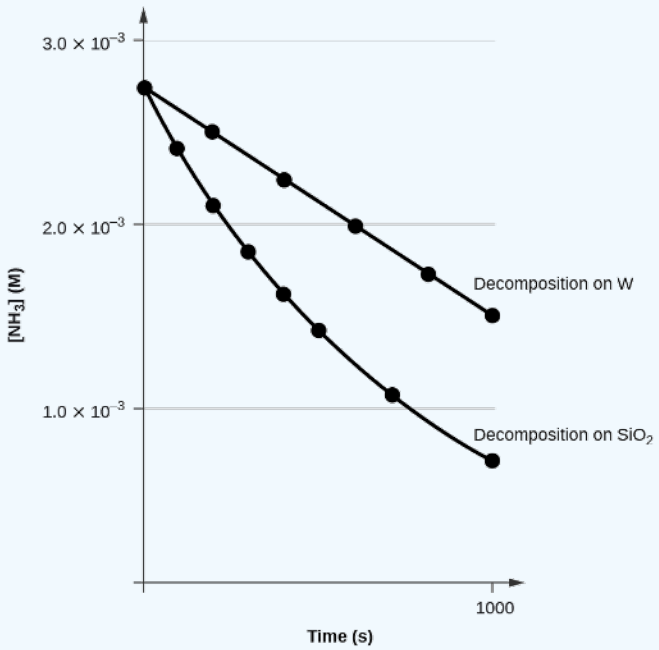


Figure **12.7.3**: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

Solution

The integrated rate law for zero-order kinetics describes a linear plot of reactant concentration, $[A]_t$, versus time, t, with a slope equal to the negative of the rate constant, $-k$. Following the mathematical approach of previous examples, the slope of the linear data plot (for decomposition on W) is estimated from the graph. Using the ammonia concentrations at t = 0 and t = 1000 s:

$$k = -\text{ slope } = -\frac{(0.0015 molL^{-1} - 0.0028 molL^{-1})}{(1000s - 0s)} = 1.3 \times 10^{-6} molL^{-1}s^{-1}$$

Exercise 12.7.5

The zero-order plot in Figure **12.7.3** shows an initial ammonia concentration of 0.0028 mol L^{-1} decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach 0.0001 mol L^{-1}?

Answer

35 min

The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide (Figure **12.7.1**) as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*;

during the third half-life, it decreases from 0.250 *M* to 0.125 *M*. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

First-Order Reactions

An equation relating the half-life of a first-order reaction to its rate constant may be derived from the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

Invoking the definition of half-life, symbolized requires that the concentration of *A* at this point is one-half its initial concentration: $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$

Substituting these terms into the rearranged integrated rate law and simplifying yields the equation for half-life:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

This equation describes an expected inverse relation between the half-life of the reaction and its rate constant, *k*. Faster reactions exhibit larger rate constants and correspondingly shorter half-lives. Slower reactions exhibit smaller rate constants and longer half-lives.

Example 12.7.6: 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 in Figure 12.7.4.



Figure 12.7.4: The decomposition of H_2O_2 at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

Inspecting the concentration/time data in Figure 12.7.4 shows the half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 s} = 3.21 \times 10^{-5} s^{-1}$$

Exercise 12.7.1

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

5.02 d.

Second-Order Reactions

Following the same approach as used for first-order reactions, an equation relating the half-life of a second-order reaction to its rate constant and initial concentration may be derived from its integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Restrict t to $t_{1/2}$

$$t = t_{1/2}$$

define $[A]_t$ as one-half $[A]_0$

$$[A]_t = \frac{1}{2}[A]_0$$

and then substitute into the integrated rate law and simplify:

$$\begin{aligned} \frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2} \\ t_{1/2} &= \frac{1}{k[A]_0} \end{aligned}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Zero-Order Reactions

As for other reaction orders, an equation for zero-order half-life may be derived from the integrated rate law:

$$[A] = -kt + [A]_0$$

Restricting the time and concentrations to those defined by half-life: and Substituting these terms into the zero-order integrated rate law yields:

$$\begin{aligned} \frac{[A]_0}{2} &= -kt_{1/2} + [A]_0 \\ kt_{1/2} &= \frac{[A]_0}{2} \\ t_{1/2} &= \frac{[A]_0}{2k} \end{aligned}$$

As for all reaction orders, the half-life for a zero-order reaction is inversely proportional to its rate constant. However, the half-life of a zero-order reaction increases as the initial concentration increases.

Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in Table **12.7.1**.

Table **12.7.1**: 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 rate constant	M s^{-1}	s^{-1}	M^{-1} s^{-1}
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	ln$[A]$ vs. t	vs. t
relationship between slope of linear plot and rate constant	k = −slope	k = −slope	k = slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Example 12.7.7: Half-Life for Zero-Order and Second-Order Reactions

What is the half-life for the butadiene dimerization reaction described in Example **12.7.3**?

Solution

The reaction in question is second order, is initiated with a 0.200 mol L^{-1} reactant solution, and exhibits a rate constant of 0.0576 L mol^{-1} min^{-1}. Substituting these quantities into the second-order half-life equation:

$$t_{1/2} = \frac{1}{[(0.0576 L mol^{-1} min^{-1})\,(0.200 mol L^{-1})]} = 86.8 \text{ min}$$

Exercise 12.7.7

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see Figure **12.7.3**)?

Answer

87 min

This page titled 12.7: Integrated Rate Laws is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.4: Integrated Rate Laws** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.8: Collision Theory

Learning Objectives

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

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\ \text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,CO\,(g) + O_2\,(g) \longrightarrow 2\,CO_2\,(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient amounts, the reaction will occur at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO\,(g) + O_2\,(g) \longrightarrow CO_2\,(g) + O\,(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure **12.8.1**. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (\ce{O=C=O}\). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

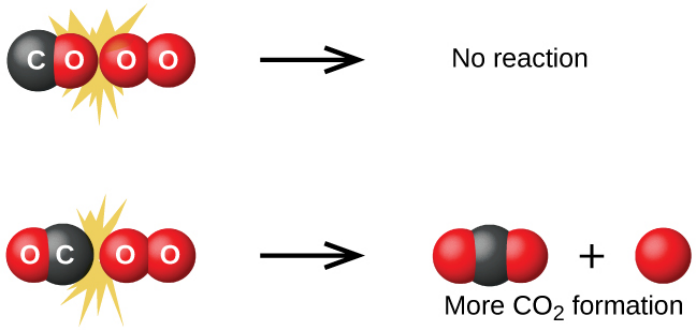


Figure 12.8.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy** (E_a). How this energy compares to the kinetic energy provided by colliding reactant molecules is a primary factor affecting the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly since only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, a large fraction of molecules will be adequately energetic and the reaction will proceed rapidly.

Figure 12.8.2 shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$\mathrm{A^+B \longrightarrow C^+D}$$

These reaction diagrams are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, $\mathrm{A+B}$. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, C + D. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

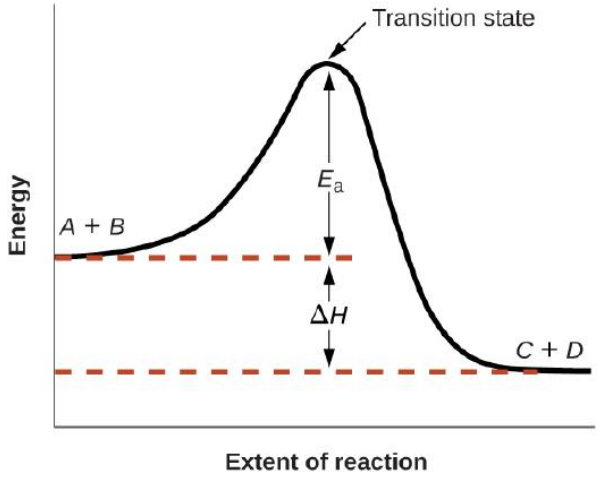


Figure 12.8.2: Reaction diagram for the exothermic reaction

The **Arrhenius equation** relates the activation energy and the rate constant, *k*, for many chemical reactions:

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

In this equation, R is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, *e* is the constant 2.7183, and *A* is a constant called the **frequency factor**, which is related to the frequency of collisions and the orientation of the reacting molecules.

Postulates of collision theory are nicely accommodated by the Arrhenius equation. The frequency factor, *A*, reflects how well the reaction conditions favor properly oriented collisions between reactant molecules. An increased probability of effectively oriented collisions results in larger values for *A* and faster reaction rates.

The exponential term, $e^{-Ea/RT}$, describes the effect of activation energy on reaction rate. According to kinetic molecular theory (see chapter on gases), the temperature of matter is a measure of the average kinetic energy of its constituent atoms or molecules. The distribution of energies among the molecules composing a sample of matter at any given temperature is described by the plot shown in Figure 12.8.3*a*. Two shaded areas under the curve represent the numbers of molecules possessing adequate energy (*RT*) to overcome the activation barriers (E_a). A lower activation energy results in a greater fraction of adequately energized molecules and a faster reaction.

The exponential term also describes the effect of temperature on reaction rate. A higher temperature represents a correspondingly greater fraction of molecules possessing sufficient energy (*RT*) to overcome the activation barrier (E_a), as shown in Figure 12.8.3*b*. This yields a greater value for the rate constant and a correspondingly faster reaction rate.

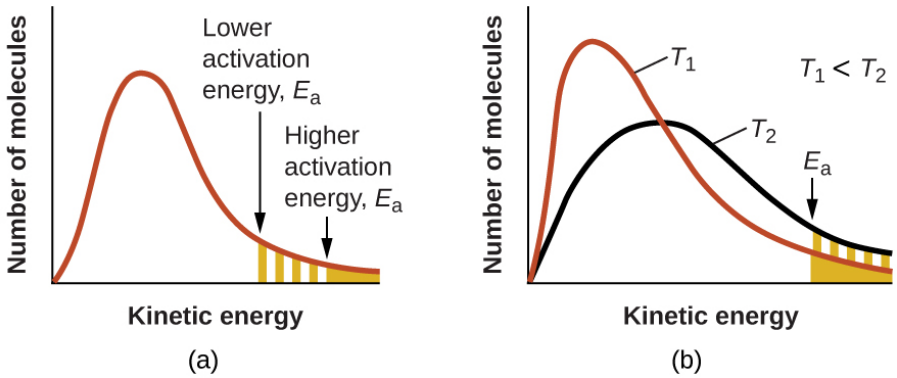


Figure 12.8.3: Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

A convenient approach for determining E_a for a reaction involves the measurement of *k* at two or more different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

A plot of $\ln k$ versus $\frac{1}{T}$ is linear with a slope equal to $\frac{-E_a}{R}$ and a y-intercept equal to $\ln A$.

Example 12.8.1: Determination of E_a

The variation of the rate constant with temperature for the decomposition of $\mathrm{HI(g)}$ to $\mathrm{H_2(g)}$ and $\mathrm{I_2(g)}$ is given here. What is the activation energy for the reaction?

$$\mathrm{2\,HI(g) \longrightarrow H_2(g) + I_2(g)}$$

T (K)	k (L/mol/s)
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

Use the provided data to derive values of $\frac{1}{T}$ and $\ln k$:

$\frac{1}{T}$	$\ln k$
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

Figure 12.8.4 is a graph of $\ln k$ versus $\frac{1}{T}$. In practice, the equation of the line (slope and *y*-intercept) that best fits these plotted data points would be derived using a statistical process called regression. This is helpful for most experimental data because a perfect fit of each data point with the line is rarely encountered. For the data here, the fit is nearly perfect and the slope may be estimated using any two of the provided data pairs. Using the first and last data points permits estimation of the slope.

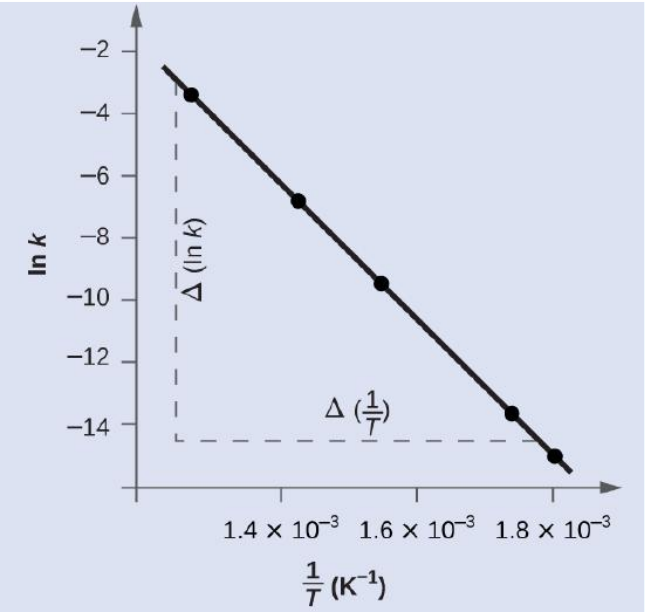


Figure **12.8.4**: This graph shows the linear relationship between $\ln k$ versus $\frac{1}{T}$ for the reaction $2HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

$$\begin{aligned}
\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\
&= \frac{(-14.860) - (-3.231)}{\left(1.80 \times 10^{-3} K^{-1}\right) - \left(1.28 \times 10^{-3} K^{-1}\right)} \\
&= \frac{-11.629}{0.52 \times 10^{-3} K^{-1}} = -2.2 \times 10^{4} K \\
&= -\frac{E_a}{R} \\
E_a &= -\text{ slope } \times R = -\left(-2.2 \times 10^{4} K \times 8.314 J mol^{-1} K^{-1}\right) \\
&\quad 1.8 \times 10^{5} J mol^{-1} \text{ or } 180 k J mol^{-1}
\end{aligned}$$

Alternative approach: A more expedient approach involves deriving activation energy from measurements of the rate constant at just two temperatures. In this approach, the Arrhenius equation is rearranged to a convenient two-point form:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Rearranging this equation to isolate activation energy yields:

$$E_a = -R\left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right)$$

Any two data pairs may be substituted into this equation—for example, the first and last entries from the above data table:

$$E_a = -8.314 J mol^{-1} K^{-1}\left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3} K^{-1} - 1.80 \times 10^{-3} K^{-1}}\right)$$

and the result is E_a = 1.8 10^5 J mol^{-1} or 180 kJ mol^{-1}

This approach yields the same result as the more rigorous graphical approach used above, as expected. In practice, the graphical approach typically provides more reliable results when working with actual experimental data.

Exercise 12.8.1

The rate constant for the rate of decomposition of $\mathbf{N_2O_5}$ to $\mathbf{NO}$ and $\mathbf{O_2}$ in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$\mathbf{2\,N_2O_5\,(g) \longrightarrow 4\,NO\,(g) + 3\,O_2\,(g)}$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer

1.1 10^5 J mol^{-1} or 110 kJ mol^{-1}

This page titled 12.8: Collision Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.5: Collision Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.9: Reaction Mechanisms

Learning Objectives

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

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes place. The reaction mechanism (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$O_3(g) \longrightarrow O_2(g) + O$$
$$O + O_3(g) \longrightarrow 2O_2(g)$$

Each of the steps in a reaction mechanism is an **elementary reaction**. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction *does not involve the direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction's equation undergo only the bond-breaking and/or making events depicted to yield the product(s). For this reason, *the rate law for an elementary reaction may be derived directly from the balanced chemical equation describing the reaction*. This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the reaction of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{products}$$

The rate law for a unimolecular reaction is first order:

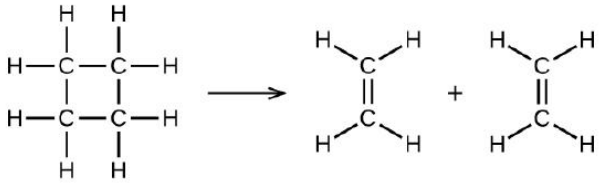
$$\text{rate} = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above. However, some unimolecular reactions may be the only step of a single-step reaction mechanism. (In other words, an "overall"

reaction may also be an elementary reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the following chemical equation:



This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$\text{rate} = -\frac{\Delta[C_4H_8]}{\Delta t} = k[C_4H_8]$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

Bimolecular Elementary Reactions

A bimolecular reaction involves two reactant species, for example:

$$A + B \longrightarrow \text{products}$$

and

$$2A \longrightarrow \text{products}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in A and first order in B (second-order overall):

$$\text{rate} = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in A:

$$\text{rate} = k[A][A] = k[A]^2$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

(see Figure **12.9.1**)



Figure **12.9.1**: The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is the second step of the two-step ozone decomposition mechanism discussed earlier in this section:

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

Termolecular Elementary Reactions

An elementary termolecular reaction involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-

thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$2NO + O_2 \longrightarrow 2NO_2$$
$$\text{rate } = k[NO]^2\,[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2NO + Cl_2 \longrightarrow 2NOCl$$
$$\text{rate } = k[NO]^2\,[Cl_2]$$

Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure **12.9.2**.



Figure **12.9.2**: A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate } = k\,[NO_2]\,[CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate } = k[NO_2]^2$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)\ \text{(slow)}$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)\ \text{(fast)}$$

The rate-determining (slower) step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

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 this step. However, when the rate-determining step is preceded by a step involving a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

As discussed in several chapters of this text, a reversible reaction is at *equilibrium* when the rates of the forward and reverse processes are equal. Consider the reversible elementary reaction in which NO dimerizes to yield an intermediate species N_2O_2.

$$NO + NO \rightleftharpoons N_2O_2$$

When this reaction is at equilibrium:

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$
$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

This expression may be rearranged to express the concentration of the intermediate in terms of the reactant NO:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

Since intermediate species concentrations are not used in formulating rate laws for overall reactions, this approach is sometimes necessary, as illustrated in the following example exercise.

Example 12.9.1: Deriving a Rate Law from a Reaction Mechanism

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:

$$\text{Step 1:} \quad \mathrm{NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g)} \quad \text{(fast)}$$
$$\text{Step 2:} \quad \mathrm{NOCl_2(g) + NO(g) \rightleftharpoons 2\,NOCl(g)} \quad \text{(slow)}$$

Use this mechanism to derive the equation and predicted rate law for the overall reaction.

Solution

The equation for the overall reaction is obtained by adding the two elementary reactions:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

To derive a rate law from this mechanism, first write rates laws for each of the two steps.

$$\text{rate}_1 = k_1[NO]\,[Cl_2] \text{ for the forward reaction of step 1}$$
$$\text{rate}_{-1} = k_{-1}[NOCl_2] \text{ for the reverse reaction of step 1}$$
$$\text{rate}_2 = k_2[NOCl_2]\,[NO] \text{ for step 2}$$

Step 2 is the rate-determining step, and so the rate law for the overall reaction should be the same as for this step. However, the step 2 rate law, as written, contains an intermediate species concentration, $[NOCl_2]$. To remedy this, use the first step's rate laws to derive an expression for the intermediate concentration in terms of the reactant concentrations.

Assuming step 1 is at equilibrium:

$$\text{rate}_1 = \text{rate}_{-1}$$
$$k_1[NO]\,[Cl_2] = k_{-1}[NOCl_2]$$
$$[NOCl_2] = \left(\frac{k_1}{k_{-1}}\right)[NO]\,[Cl_2]$$

Substituting this expression into the rate law for step 2 yields:

$$\text{rate}_2 = \text{rate}_{\text{overall}} = \left(\frac{k_2k_1}{k_{-1}}\right)[NO]^2\,[Cl_2]$$

Exercise 12.9.1

The first step of a proposed multistep mechanism is:

\[\ce{F2(g) <=> 2 F(g) \tag{fast} \]

Derive the equation relating atomic fluorine concentration to molecular fluorine concentration.

Answer

$$[\mathrm{F}] = \left(\frac{k_1 [F_2]}{k_{-1}}\right)^{1/2}$$

This page titled 12.9: Reaction Mechanisms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.6: Reaction Mechanisms** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.10: Catalysis

Learning Objectives

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

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure **12.10.1** shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

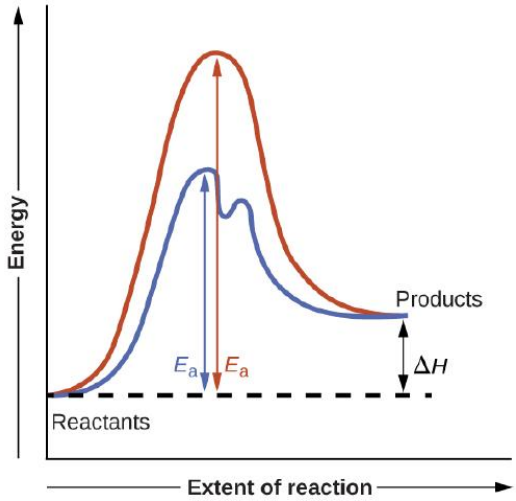
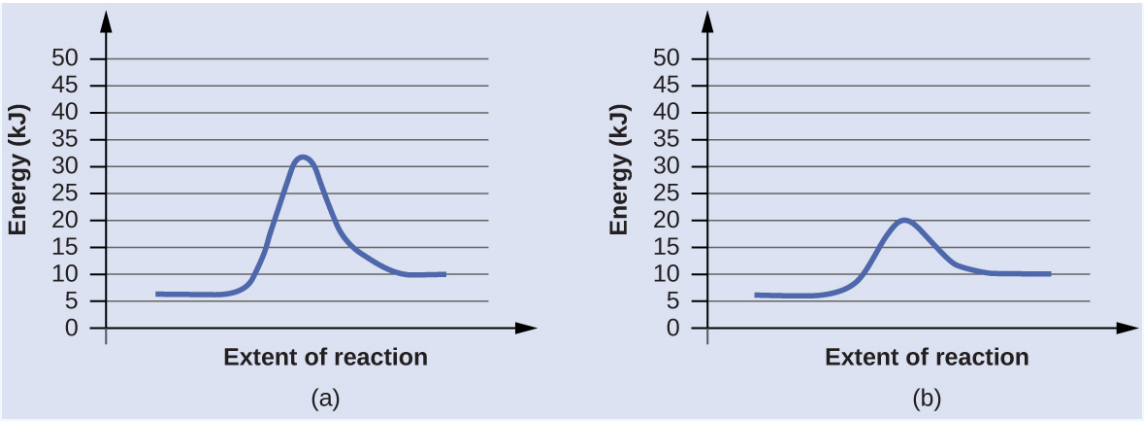


Figure **12.10.1**: Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 12.10.1: Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

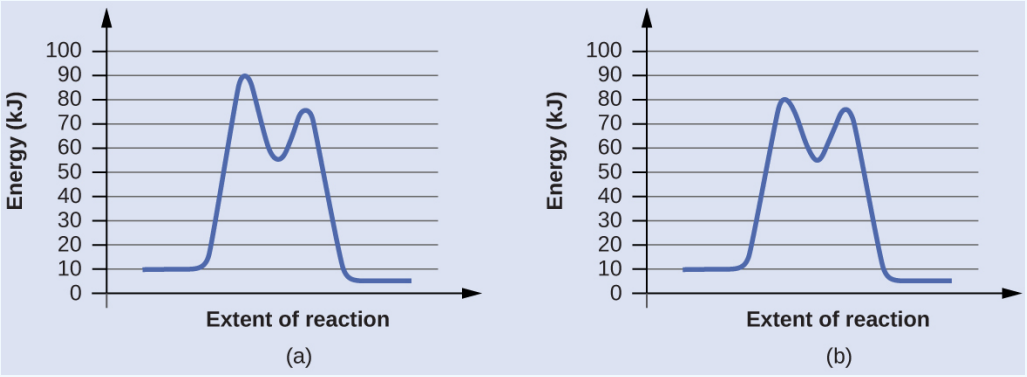
Activation energies are calculated by subtracting the reactant energy from the transition state energy.

$$\text{diagram}(a): E_a = 32kJ - 6kJ = 26kJ$$
$$\text{diagram}(b): E_a = 20kJ - 6kJ = 14kJ$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram b.

? Exercise 12.10.1

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3O_2(g) \xrightarrow{h\nu} 2O_3(g)$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following two-step mechanism:

$$O_3 \longrightarrow O_2 + O$$
$$O + O_3 \longrightarrow 2O_2$$

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide–catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$
$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$$

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

Portrait of a Chemist: Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure **12.10.2**), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[1] Molina's initial discovery of stratospheric depletion of ozone by chlorine atoms was done at the University of California Irvine, he later moved to the NASA/Jet Propulsion Laboratory, MIT and the University of California, San Diego. At the time of his death in 2020 Molina, a Mexican citizen had established a new center for the study of energy and the environment in Mexico City.

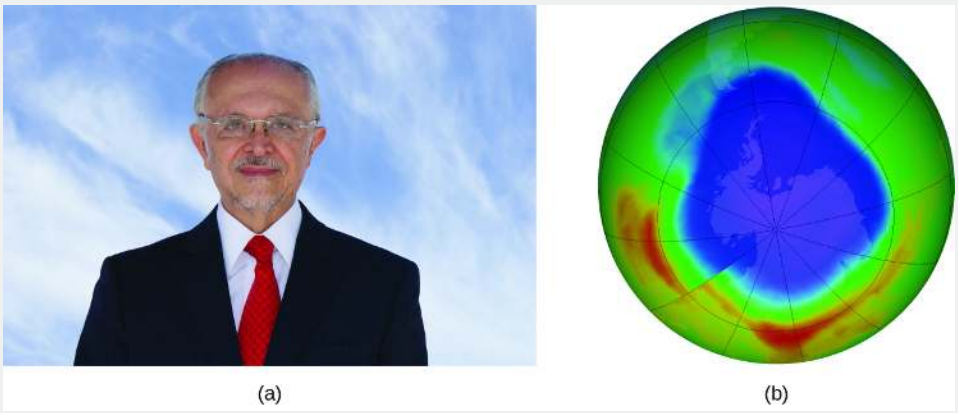


Figure **12.10.2**: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his (b) early research on stratospheric depletion of ozone and later the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

$$CH_3Cl + OH \longrightarrow Cl + \text{other products} \tag{12.10.1}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$

overall Reaction: $O_3 + O \longrightarrow 2O_2$ \nonumber \]

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 12.21, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure **12.10.4**).

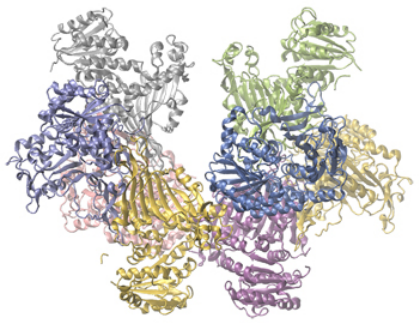


Figure 12.21 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

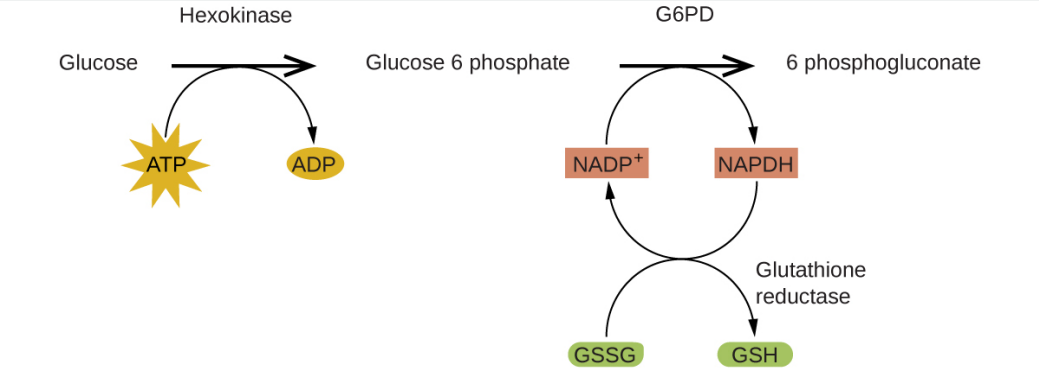


Figure **12.10.4**: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)
3. Reaction of the adsorbed reactant(s)

Figure **12.10.5**: illustrates the steps of a mechanism for the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

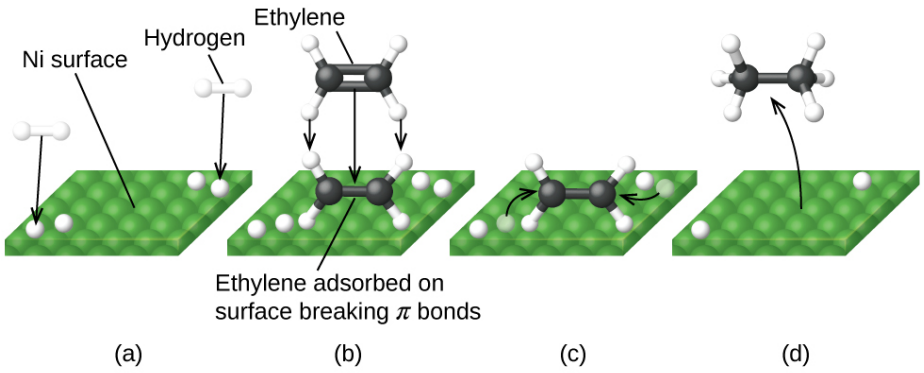


Figure **12.10.5**: Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C–C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.

Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure **12.10.6**).

Chemistry in Everyday Life: Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure **12.10.6**).

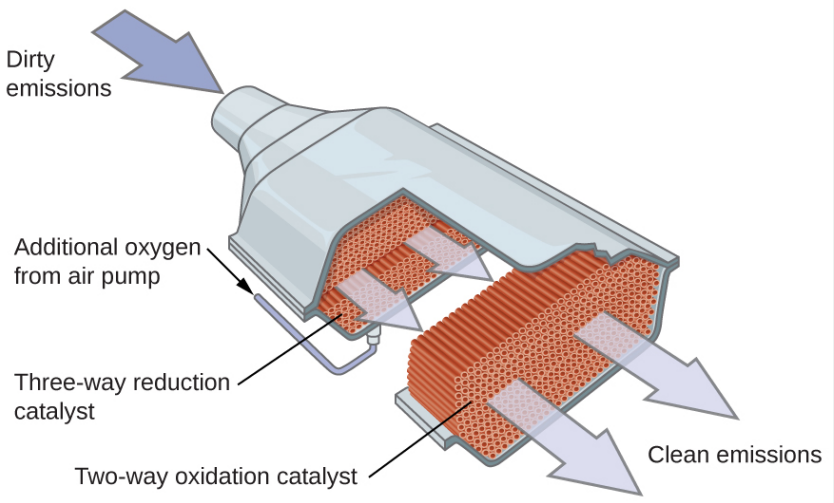


Figure **12.10.6**: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Link to Learning

The LibreTexts provides a thorough explanation of how catalytic converters work.

How Sciences Interconnect: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table **12.10.1**.

Table **12.10.1**: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain

how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure **12.10.7**).

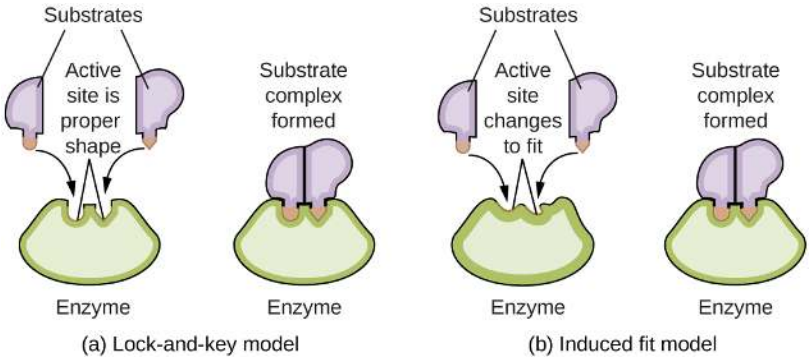


Figure **12.10.7**: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

Footnotes

- 1"The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

This page titled 12.10: Catalysis is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **12.7: Catalysis** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

12.11: Key Terms

activated complex | (also, transition state) unstable combination of reactant species formed during a chemical reaction

activation energy (E_a) | minimum energy necessary in order for a reaction to take place

Arrhenius equation | mathematical relationship between a reaction's rate constant, activation energy, and temperature

average rate | rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

bimolecular reaction | elementary reaction involving two reactant species

catalyst | substance that increases the rate of a reaction without itself being consumed by the reaction

collision theory | model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

elementary reaction | reaction that takes place in a single step, precisely as depicted in its chemical equation

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

half-life of a reaction ($t_{1/2}$) | time required for half of a given amount of reactant to be consumed

heterogeneous catalyst | catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst | catalyst present in the same phase as the reactants

initial rate | instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

instantaneous rate | rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

integrated rate law | equation that relates the concentration of a reactant to elapsed time of reaction

intermediate | species produced in one step of a reaction mechanism and consumed in a subsequent step

method of initial rates | common experimental approach to determining rate laws that involves measuring reaction rates at varying initial reactant concentrations

molecularity | number of reactant species involved in an elementary reaction

overall reaction order | sum of the reaction orders for each substance represented in the rate law

rate constant (k) | proportionality constant in a rate law

rate expression | mathematical representation defining reaction rate as change in amount, concentration, or pressure of reactant or product species per unit time

rate law | (also, rate equation) (also, differential rate laws) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

rate of reaction | measure of the speed at which a chemical reaction takes place

rate-determining step | (also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction diagram | used in chemical kinetics to illustrate various properties of a reaction

reaction mechanism | stepwise sequence of elementary reactions by which a chemical change takes place

reaction order | value of an exponent in a rate law (for example, zero order for 0, first order for 1, second order for 2, and so on)

termolecular reaction | elementary reaction involving three reactant species

unimolecular reaction | elementary reaction involving a single reactant species

12.11: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **12.8: Key Terms** is licensed CC BY 4.0.

12.12: Key Equations

integrated rate law for zero-order reactions:
half-life for a zero-order reaction
integrated rate law for first-order reactions:
half-life for a first-order reaction
integrated rate law for second-order reactions:
half-life for a second-order reaction

12.12: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **12.9: Key Equations** is licensed CC BY 4.0.

CHAPTER OVERVIEW

13: Fundamental Equilibrium Concepts

In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

13.1: Introduction
13.2: Chemical Equilibria
13.3: Equilibrium Constants
13.4: Shifting Equilibria - Le Chatelier’s Principle
13.5: Equilibrium Calculations
13.6: Key Terms
13.7: Key Equations
13.8: Summary
13.9: Exercises

This page titled 13: Fundamental Equilibrium Concepts is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

13.1: Introduction

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot, they enter the surf to swim and cool off. As the swimmers tire, they return to the beach to rest. If the rate at which sunbathers enter the surf were to equal the rate at which swimmers return to the sand, then the numbers (though not the identities) of sunbathers and swimmers would remain constant. This scenario illustrates a dynamic phenomenon known as *equilibrium*, in which opposing processes occur at equal rates. Chemical and physical processes are subject to this phenomenon; these processes are at equilibrium when the forward and reverse reaction rates are equal. Equilibrium systems are pervasive in nature; the various reactions involving carbon dioxide dissolved in blood are examples (see Figure **13.1.1**). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

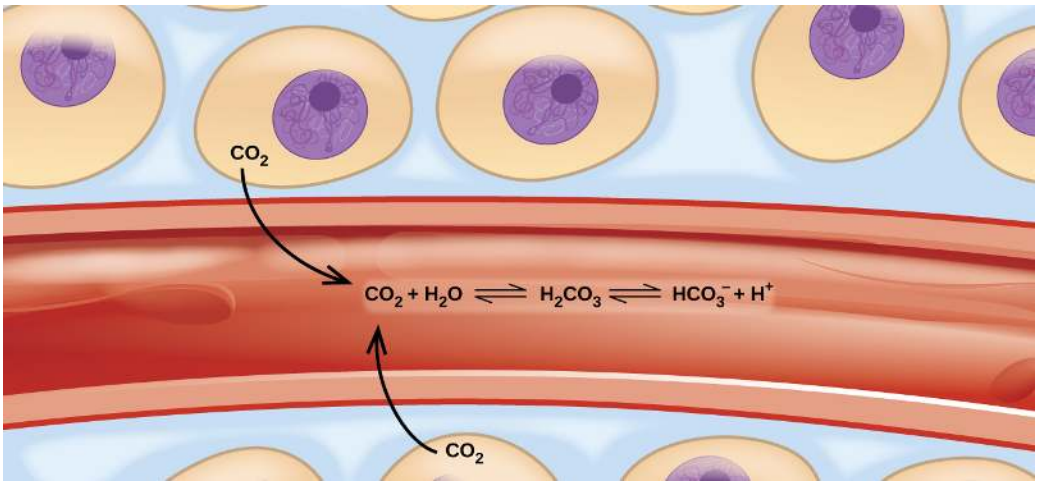


Figure **13.1.1**: Transport of carbon dioxide in the body involves several reversible chemical reactions, including hydrolysis and acid ionization (among others).

This page titled 13.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **13.0: Introduction** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.2: Chemical Equilibria

Learning Objectives

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

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium
- Relate the magnitude of an equilibrium constant to properties of the chemical system

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of “reactant” and “product,” a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

Figure 13.2.1 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Note that a special double arrow is used to emphasize the reversible nature of the reaction.

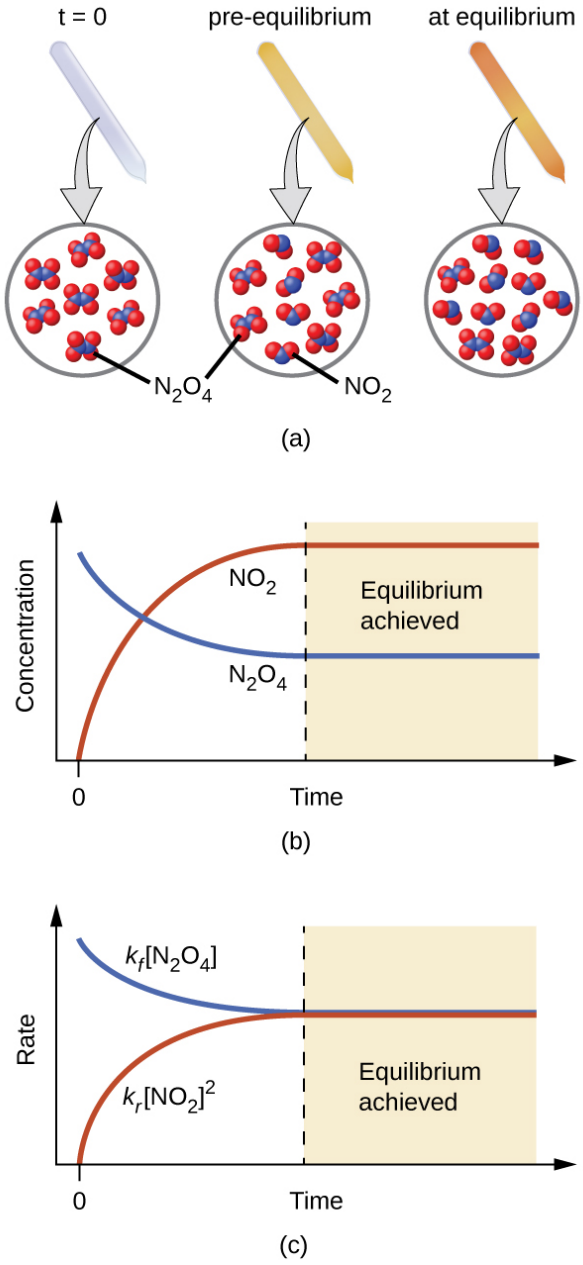


Figure **13.2.1**: (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\text{rate}_f = k_f\,[N_2O_4]$$

$$\text{rate}_r = k_r[NO_2]^2$$

As the reaction begins (t = 0), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (Figure **13.2.1***b*). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure **13.2.1***c*). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure **13.2.1***b* and Figure **13.2.1***c*). It's

important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not “stopped,” but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.



Figure **13.2.2**: 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 may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\mathrm{Br_2\,(l)} \rightleftharpoons \mathrm{Br_2\,(g)}$$

When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in Figure **13.2.3**.



Figure **13.2.3**: A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

This page titled 13.2: Chemical Equilibria is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **13.1: Chemical Equilibria** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.3: Equilibrium Constants

Learning Objectives

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

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

The status of a reversible reaction is conveniently assessed by evaluating its reaction quotient (Q). For a reversible reaction described by

$$mA + nB + \rightleftharpoons xC + yD$$

the reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

where the subscript c denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Q_p = \frac{P_C^x P_D^y}{P_A{}^m P_B{}^n}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing Q. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

Example 13.3.1: Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient 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. $$Q_c = \frac{[O_3]^2}{[O_2]^3}$$

b. $$Q_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

c. $$Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

Exercise 13.3.1

Write the concentration-based reaction quotient 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

a. $$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

b. $$Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$$

c. $$Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$$

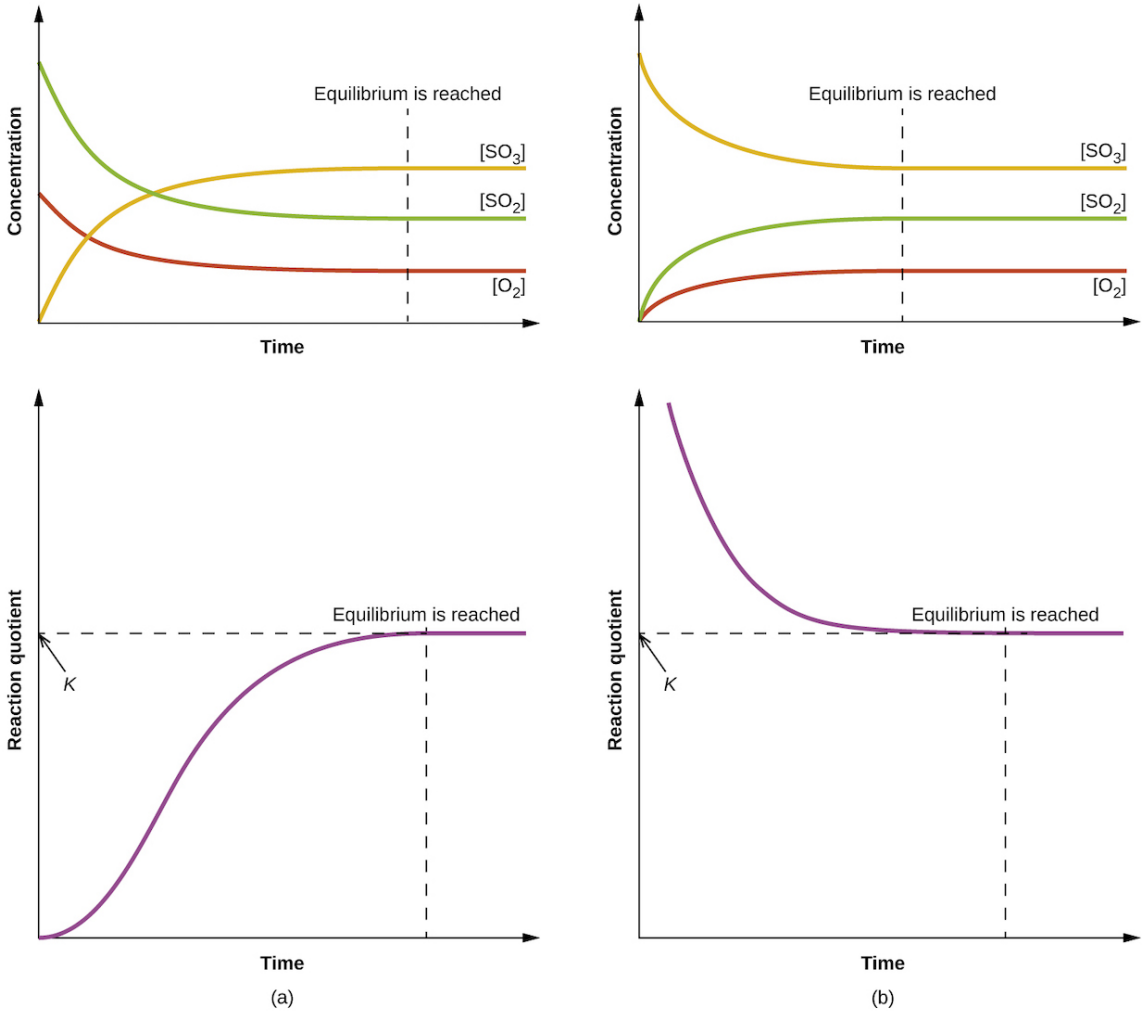


Figure **13.3.1** Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

Two different experimental scenarios are depicted in Figure **13.3.1**, one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{0^2}{[SO_2]^2\,[O_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[SO_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the equilibrium constant, K:

$$K \equiv Q \text{ at equilibrium}$$

Comparison of the data plots in Figure **13.3.1** shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**.

Definition: Law of Mass Action

At a given temperature, the reaction quotient for a system at equilibrium is constant.

Example 13.3.2: 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

As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(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 13.3.2

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

K_c = 4.3

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large *K* will reach equilibrium when most of the reactant has been converted to product, whereas a small *K* indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of *K* does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing *Q* to *K* for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

To further illustrate this important point, consider the reversible reaction shown below:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) \quad K_c = 0.640 \quad T = 800°C$$

The bar charts in Figure **13.3.2** represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.

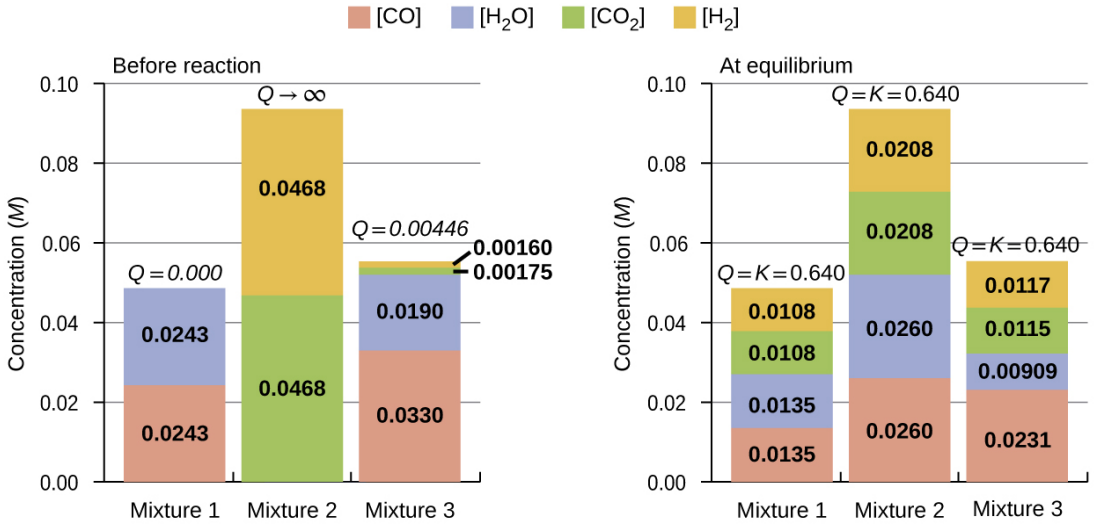


Figure **13.3.2**: Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction

Example 13.3.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) \quad K_c = 0.64$$

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*
$[CO_2]_i$	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 13.3.3

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 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \quad K_c = 0.060$$

c. 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

(a) Q_c = 6.45 \times 10^{3} DELMAR, forward. (b) Q_c = 0.23, reverse. (c) Q_c = 0, forward.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$\mathrm{C_2H_2\,(aq) + 2\,Br_2\,(aq) \rightleftharpoons C_2H_2Br_4\,(aq)} \qquad K_c = \frac{[C_2H_2Br_4]}{[C_2H_2]\,[Br_2]^2}$$

$$\mathrm{I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3^-\,(aq)} \qquad K_c = \frac{[I_3-}{[I_2]\,[I^-]}$$

$$\mathrm{HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)} \qquad K_c = \frac{[H_3O^+]\,[F^-]}{[HF]}$$

$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \qquad K_c = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the Q (or K) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

> **Note**
>
> It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

The equilibria below all involve gas-phase solutions:

$$\mathrm{C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)} \qquad K_c = \frac{[C_2H_4]\,[H_2]}{[C_2H_6]}$$

$$\mathrm{3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)} \qquad K_c = \frac{[O_3]^2}{[O_2]^3}$$

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \qquad K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$\mathrm{C_3H_8\,(g) + 5\,O_2\,(g) \rightleftharpoons 3\,CO_2\,(g) + 4\,H_2O\,(g)} \qquad K_c = \frac{[CO_2]^3[H_2O]^4}{[C_3H_8]\,[O_2]^5}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

$$PV = nRT$$
$$P = \left(\frac{n}{V}\right)RT$$
$$= MRT$$

where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$K_P = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$
$$= \frac{([C] \times RT)^c ([D] \times RT)^d}{([A] \times RT)^a ([B] \times RT)^b}$$
$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}}$$
$$= K_c (RT)^{(c+d)-(a+b)}$$
$$= K_c (RT)^{\Delta n}$$

And so, the relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n}$$

where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\Delta n = (c + d) - (a + b)$$

Example 13.3.4: 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. $\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$
d. 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

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. $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = \frac{K_c}{(RT)^2}$$

d.
$$K_P = K_c (RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$$

Exercise 13.3.4

Write the equations relating K_c to K_P for each of the following reactions:

a. $\mathrm{2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)}$
b. $\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$
c. $\mathrm{C_3H_8\,(g) + 5\,O_2\,(g) \rightleftharpoons 3\,CO_2\,(g) + 4\,H_2O\,(g)}$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$\mathrm{CH_3OH\,(g) \rightleftharpoons CO\,(g) + 2\,H_2\,(g)}$$

What would be the value of K_P at this temperature?

Answer

(a) $K_P = K_c\,(RT)^{-1}$; (b) $K_P = K_c\,(RT)$; (c) $K_P = K_c\,(RT)$; (d) 160 or 1.6 \times 10^{2} DELMAR

Heterogeneous Equilibria

A heterogeneous equilibrium involves reactants and products in two or more different phases, as illustrated by the following examples:

$$\mathrm{PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,Cl^-\,(aq)} \qquad K_c = \left[\mathrm{Pb^{2+}}\right]\left[\mathrm{Cl^-}\right]^2$$

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightleftharpoons CaCO_3\,(s)} \qquad K_c = \frac{1}{[\mathrm{CO_2}]}$$

$$\mathrm{C\,(s) + 2\,S\,(g) \rightleftharpoons CS_2\,(g)} \qquad K_c = \frac{[CS_2]}{[\mathrm{S}^2}$$

$$\mathrm{Br_2\,(l) \rightleftharpoons Br_2\,(g)} \qquad K_c = [\mathrm{Br_2\,(g)}]$$

Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.

Two of the above examples include terms for gaseous species only in their equilibrium constants, and so K_p expressions may also be written:

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightleftharpoons CaCO_3\,(s)} \qquad K_P = \frac{1}{P_{\mathrm{CO_2}}}$$

$$\mathrm{C\,(s) + 2\,S\,(g) \rightleftharpoons CS_2\,(g)} \qquad K_P = \frac{P_{\mathrm{CS_2}}}{\left(P_{\mathrm{S}}\right)^2}$$

Coupled Equilibria

The equilibrium systems discussed so far have all been relatively simple, involving just single reversible reactions. Many systems, however, involve two or more *coupled* equilibrium reactions, those which have in common one or more reactant or product species. Since the law of mass action allows for a straightforward derivation of equilibrium constant expressions from balanced chemical equations, the K value for a system involving coupled equilibria can be related to the K values of the individual reactions. Three basic manipulations are involved in this approach, as described below.

1. Changing the direction of a chemical equation essentially swaps the identities of “reactants” and “products,” and so the equilibrium constant for the reversed equation is simply the reciprocal of that for the forward equation.

$$A \rightleftharpoons B \quad K_c = \frac{[B]}{[A]}$$

$$B \rightleftharpoons A \quad K_{c'} = \frac{[A]}{[B]}$$

$$K_{c'} = \frac{1}{K_c}$$

2. Changing the stoichiometric coefficients in an equation by some factor x results in an exponential change in the equilibrium constant by that same factor:

$$A \rightleftharpoons B \qquad K_c = \frac{[B]}{[A]}$$

$$xA \rightleftharpoons xB \quad K_c = \frac{[B]^x}{[A]^x}$$

$$K_{c'} = {K_c}^x$$

3. Adding two or more equilibrium equations together yields an overall equation whose equilibrium constant is the mathematical product of the individual reaction’s K values:

$$A \rightleftharpoons B \quad K_{c1} = \frac{[B]}{[A]}$$

$$B \rightleftharpoons C \quad K_{c2} = \frac{[C]}{[B]}$$

The net reaction for these coupled equilibria is obtained by summing the two equilibrium equations and canceling any redundancies:

$$A + B \rightleftharpoons B + C$$
$$A + B \rightleftharpoons B + C$$
$$A \rightleftharpoons C$$

$$K_{c'} = \frac{[C]}{[A]}$$

Comparing the equilibrium constant for the net reaction to those for the two coupled equilibrium reactions reveals the following relationship:

$$K_{c1}K_{c2} = \frac{[B]}{[A]} \times \frac{[C]}{[B]} = \frac{\cancel{[B]}\,[C]}{[A]\,\cancel{[B]}} = \frac{[C]}{[A]} = K_{c'}$$

$$K_{c'} = K_{c1}K_{c2}$$

Example **13.3.5** demonstrates the use of this strategy in describing coupled equilibrium processes.

Example 13.3.5: Equilibrium Constants for Coupled Reactions

A mixture containing nitrogen, hydrogen, and iodine established the following equilibrium at 400 °C:

$$2\,NH_3\,(g) + 3\,I_2\,(g) \rightleftharpoons N_2\,(g) + 6\,HI\,(g)$$

Use the information below to calculate Kc for this reaction.

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) K_{c1} = 0.50 \text{ at } 400°C$$
$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) K_{c2} = 50 \text{ at } 400°C$$

Solution

The equilibrium equation of interest and its K value may be derived from the equations for the two coupled reactions as follows.

Reverse the first coupled reaction equation:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \quad K_{c1}{}' = \frac{1}{K_{c1}} = \frac{1}{0.50} = 2.0$$

Multiply the second coupled reaction by 3:

$$3H_2(g) + 3I_2(g) \rightleftharpoons 6HI(g) \quad K_{c2}{}' = K_{c2}^3 = 50^3 = 1.2 \times 10^5$$

Finally, add the two revised equations:

$$2\,NH_3\,(g) + 3\,H_2\,(g) + 3\,I_2\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g) + 6\,HI\,(g)$$
$$2\,NH_3\,(g) + 3\,I_2\,(g) \rightleftharpoons N_2\,(g) + 6\,HI\,(g)$$

$$K_c = K_{c1}, K_{c2}, = (2.0)\left(1.2 \times 10^5\right) = 2.5 \times 10^5$$

Exercise 13.3.5

Use the provided information to calculate Kc for the following reaction at 550 °C:

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g) \qquad K_c = ?$$
$$CoO\,(s) + CO\,(g) \rightleftharpoons Co(s) + CO_2\,(g) \qquad K_{c1} = 490$$
$$CoO\,(s) + H_2\,(g) \rightleftharpoons Co(s) + H_2O\,(g) \qquad K_{c1} = 67$$

Answer

$K_c = 0.14$

This page titled 13.3: Equilibrium Constants is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **13.2: Equilibrium Constants** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.4: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

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

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by **Le Chatelier's principle**

Definition: Le Chatelier's Principle

if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.

Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \quad K_c = 50.0 \text{ at } 400^\circ C$$

The rate laws for the forward and reverse reactions are

$$\begin{aligned} &\text{forward} \quad \mathrm{H_2\,(g) + I_2\,(g)} \rightarrow \mathrm{2\,HI\,(g)} && \text{rate}_f = k_f[\mathrm{H_2}]^m[\mathrm{I_2}]^n \\ &\text{reverse} \quad \mathrm{2\,HI\,(g)} \rightarrow \mathrm{H_2\,(g) + I_2\,(g)} && \text{rate}_r = k_r[\mathrm{HI}]^x \end{aligned}$$

When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\text{rate}_f = \text{rate}_r$$

If the system is stressed by adding reactant, either $\mathrm{H_2}$ or $\mathrm{I_2}$, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\text{rate}_f > \text{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (the equilibrium will shift right). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\text{rate}_f < \text{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}]\,[\mathrm{I_2}]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Q_c < K_c$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2 and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2. Finally, if HI is removed, the concentrations of all three species will be lower when equilibrium is reestablished. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Q_c > K_c$ and the equilibrium will shift left.For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure P of an ideal gas is proportional to its molar concentration M,

$$M = \frac{n}{V} = \frac{P}{RT}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since

all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry 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 occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$\begin{aligned} Q_p{}' &= \frac{(3P_{HI})^2}{3P_{H_2} 3P_{I_2}} = \frac{9P_{H^2}}{9P_{H_2}P_{I_2}} = \frac{P_{HI^2}}{P_{H_2}P_{I_2}} \\ &= Q_P = K_P \end{aligned}$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system,

$$\mathrm{2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)}$$

however, yields a different result:

$$\begin{aligned} Q_P &= \frac{(P_{NO})^2}{(P_{O_2})}(P_{NO_2})^2 \\ Q'_P &= \frac{(3P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{3(P_{\mathrm{NO_2}})^2} = \frac{9(P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{9(P_{\mathrm{NO_2}})^2} = \frac{27(P_{\mathrm{NO}})^2 P_{\mathrm{O_2}}}{9(P_{\mathrm{NO_2}})^2} \\ &= 3Q_P > K_P \end{aligned}$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products 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, a change in volume will shift the equilibrium in a direction that better “accommodates” the volume change. In the second example, two moles of reactant (NO_2)

yield three moles of product ($2NO + O_2$), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

Link to Learning

Check out this link to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

Chemistry in Everyday Life: Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestley's approach involved production of carbon dioxide by reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

$$\textbf{dissolution} \qquad CO_2(g) \rightleftharpoons CO_2(aq)$$

$$\textbf{hydrolysis} \qquad CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$\textbf{ionization} \qquad H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to

the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

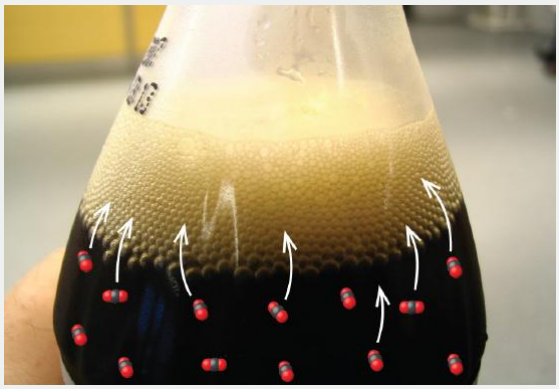


Figure 13.4.1: Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by "D Coetzee"/Flickr)

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $CO_2(aq)$ concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."

Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the

equilibrium constant, K. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$A \rightleftharpoons B$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\text{rate}_f = k_f[A]$$
$$\text{rate}_r = k_r[B]$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$k_f[A] = k_r[B]$$
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as

described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)} \quad \Delta H = +57.20\ \mathrm{kJ}$$

For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:

$$\mathrm{heat + N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$$

Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

Effect of a Catalyst

The kinetics chapter of this text identifies a *catalyst* as a substance that enables a reaction to proceed via a different mechanism with an accelerated rate. The catalyzed reaction mechanism involves a lower energy transition state than the uncatalyzed reaction, resulting in a lower activation energy, E_a, and a correspondingly greater rate constant.

To discern the effect of catalysis on an equilibrium system, consider the reaction diagram for a simple one-step (elementary) reaction shown in Figure 13.4.2. The lowered transition state energy of the catalyzed reaction results in lowered activation energies for both the forward and the reverse reactions. Consequently, both forward and reverse reactions are accelerated, and equilibrium is achieved more quickly *but without a change in the equilibrium constant*.

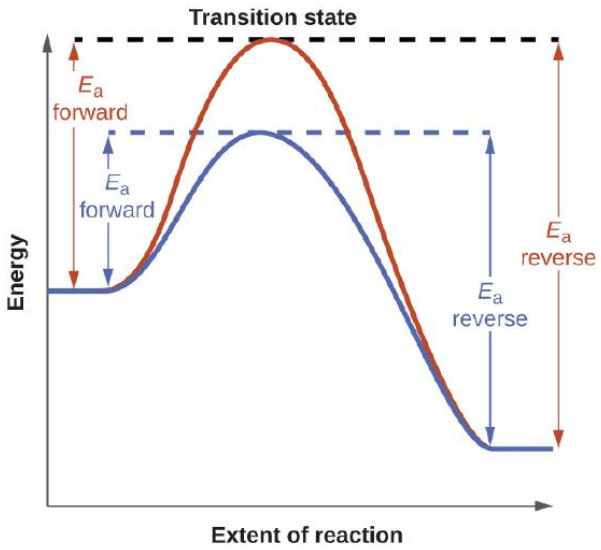


Figure **13.4.2** : Reaction diagrams for an elementary process in the absence (red) and presence (blue) of a catalyst. The presence of catalyst lowers the activation energies of both the forward and reverse reactions but does not affect the value of the equilibrium constant.

An interesting case study highlighting these equilibrium concepts is the industrial production of ammonia, NH_3. This substance is among the "top 10" industrial chemicals with regard to production, with roughly two billion pounds produced annually in the US. Ammonia is used as a chemical feedstock to synthesize a wide range of commercially useful compounds, including fertilizers, plastics, dyes, and explosives.

Most industrial production of ammonia uses the Haber-Bosch process based 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 traits of this reaction present challenges to its use in an efficient industrial process. The equilibrium constant is relatively small (Kp on the order of 10^{-5} at 25 °C), meaning very little ammonia is present in an equilibrium mixture. Also, the rate of this reaction is relatively slow at low temperatures. To raise the yield of ammonia, the industrial process is designed to operate under conditions favoring product formation:

- High pressures (concentrations) of reactants are used, ~150−250 atm, to shift the equilibrium right, favoring product formation.
- Ammonia is continually removed (collected) from the equilibrium mixture during the process, lowering its concentration and also shifting the equilibrium right.
- Although low temperatures favor product formation for this exothermic process, the reaction rate at low temperatures is inefficiently slow. A catalyst is used to accelerate the reaction to reasonable rates at relatively moderate temperatures (400−500 °C).

A diagram illustrating a typical industrial setup for production of ammonia via the Haber-Bosch process is shown in Figure **13.4.3**.

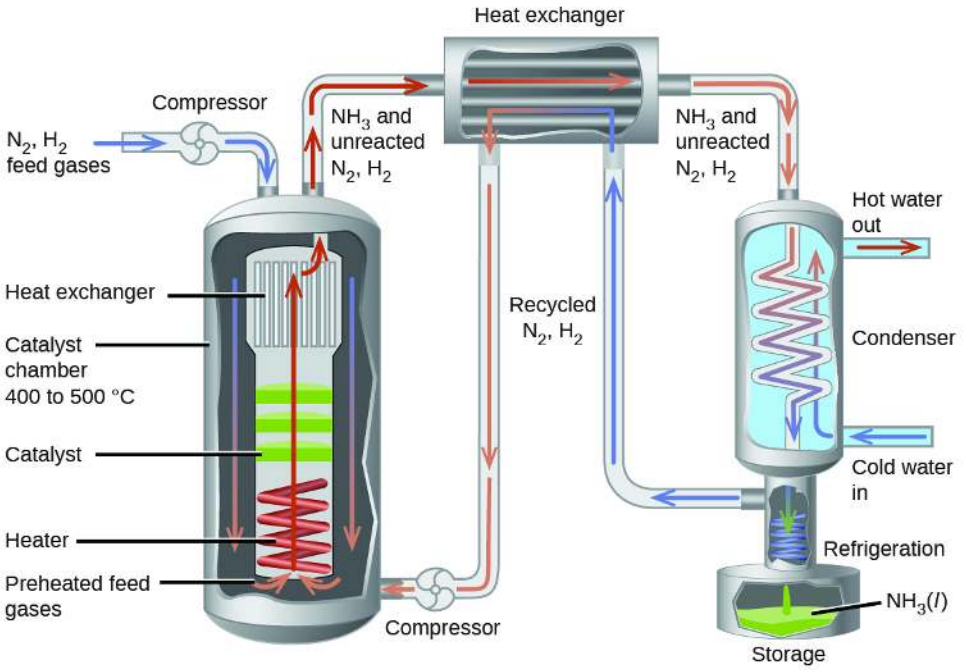


Figure **13.4.3**: The figure shows a typical industrial setup for the commercial production of ammonia by the Haber-Bosch process. The process operates under conditions that stress the chemical equilibrium to favor product formation.

This page titled 13.4: Shifting Equilibria - Le Chatelier's Principle is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **13.3: Shifting Equilibria - Le Chatelier's Principle** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.5: Equilibrium Calculations

Learning Objectives

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

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology—for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

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

As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either NH_3 only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial composition, a reaction mixture will show the same relationships between changes in the concentrations of the three species involved, as dictated by the reaction stoichiometry (see also the related content on expressing reaction rates in the chapter on kinetics). For example, if the nitrogen concentration increases by an amount x:

$$\Delta\,[N_2] = +x$$

the corresponding changes in the other species concentrations are

$$\Delta\,[\mathrm{H_2}] = \Delta\,[\mathrm{N_2}]\left(\frac{3\ \mathrm{mol\ H_2}}{1\ \mathrm{mol\ N_2}}\right) = +3x$$

$$\Delta\,[\mathrm{NH_3}] = -\Delta\,[\mathrm{N_2}]\left(\frac{2\ \mathrm{mol\ NH_3}}{1\ \mathrm{mol\ N_2}}\right) = -2x$$

where the negative sign indicates a decrease in concentration.

Example 13.5.1: Determining Relative Changes in Concentration

Derive the missing terms representing concentration changes for each of the following reactions.

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. $\underset{x}{\mathrm{C_3H_8\,(g)}} + 5\,\underset{5x}{\mathrm{O_2\,(g)}} \rightleftharpoons 3\,\underset{-3x}{\mathrm{CO_2\,(g)}} + 4\,\underset{-4x}{\mathrm{H_2O\,(g)}}$

Exercise 13.5.1

Complete the changes in concentrations for each of the following reactions:

a. $$\underset{?}{2\,SO_2\,(g)} + \underset{x}{O_2\,(g)} \rightleftharpoons \underset{?}{2\,SO_3\,(g)}$$

b. $$\underset{?}{C_4H_8\,(g)} \rightleftharpoons \underset{-2x}{2\,C_2H_4\,(g)}$$

c. $$\underset{?}{4\,NH_3\,(g)} + \underset{x}{7\,O_2\,(g)} \rightleftharpoons \underset{?}{4\,NO_2\,(g)} + \underset{?}{6\,H_2O\,(g)}$$

Answer

(a) 2*x*, *x*, −2*x*; (b) *x*, −2*x*; (c) 4*x*, 7*x*, −4*x*, −6*x* or −4*x*, −7*x*, 4*x*, 6*x*

Calculation of an Equilibrium Constant

The equilibrium constant for a reaction is calculated from the equilibrium concentrations (or pressures) of its reactants and products. If these concentrations are known, the calculation simply involves their substitution into the K expression, as was illustrated by Example **13.5.1**. A slightly more challenging example is provided next, in which the reaction stoichiometry is used to derive equilibrium concentrations from the information provided. The basic strategy of this computation is helpful for many types of equilibrium computations and relies on the use of terms for the reactant and product concentrations *initially* present, for how they *change* as the reaction proceeds, and for what they are when the system reaches *equilibrium*. The acronym ICE is commonly used to refer to this mathematical approach, and the concentrations terms are usually gathered in a tabular format called an ICE table.

Example 13.5.2: Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3^-\,(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, equilibrium concentrations are needed for all the reactants and products:

$$K_C = \frac{[I_3^-]}{[I_2]\,[I^-]}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of the reactants, presenting all the information in an ICE table.

	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 I_2 is 6.61×10^{-4} M so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$
$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$
$$= 3.39 \times 10^{-4} M$$

The ICE table may now be updated with numerical values for all its concentrations:

	$I_2 + I^- \rightleftharpoons I_3^-$		
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:

$$K_c = \frac{[I_3^-]}{[I_2]\,[I^-]}$$

$$= \frac{3.39 \times 10^{-4} M}{(6.61 \times 10^{-4} M)\,(6.61 \times 10^{-4} M)} = 776$$

Exercise 13.5.2

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is a solute in this reaction.)

Answer

$K_c = 4$

Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example exercise.

Example 13.5.3: 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,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

is 4.1×10^{-4}. Calculate the equilibrium concentration of NO(*g*) in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and 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]:

$$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$$

$$[NO]^2 = K_c\,[N_2]\,[O_2]$$

$$[NO] = \sqrt{K_c\,[N_2]\,[O_2]}$$

$$= \sqrt{\left(4.1 \times 10^{-4}\right)(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for *K*:

$$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$$

$$= \frac{\left(3.6 \times 10^{-4}\right)^2}{(0.036)(0.0089)}$$

$$= 4.0 \times 10^{-4}$$

This result is consistent with the provided value for *K* within nominal uncertainty, differing by just 1 in the least significant digit's place.

? Exercise 13.5.3

The equilibrium constant K_c for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Answer

1.53 mol/L

Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived 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. Develop an ICE table.
3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.
4. Confirm the calculated equilibrium concentrations.

The last two example exercises of this chapter demonstrate the application of this strategy.

✓ Example 13.5.4: Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant K_c for the decomposition of $PCl_5\,(g)$ into $PCl_3\,(g)$ and $Cl_2\,(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 in a mixture that initially contained only PCl_5 at a concentration of 1.00 *M*?

Solution

Use the stepwise process described earlier.

Step 1.

Determine the direction the reaction proceeds.

The balanced equation for the decomposition of PCl_5 is

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Because only the reactant is present initially $Q_c = 0$ and the reaction will proceed to the right.

Step 2:

Develop an ICE table.

	$PCl_5 \rightleftharpoons$	PCl_3	+ Cl_2
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	x	x

Step 3.

Solve for the change and the equilibrium concentrations.

Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$\begin{aligned} K_c &= \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = 0.0211 \\ &= \frac{(x)(x)}{(1.00 - x)} \\ 0.0211 &= \frac{(x)(x)}{(1.00 - x)} \\ 0.0211(1.00 - x)7 &= x^2 \\ x^2 + 0.0211x - 0.0211 &= 0 \end{aligned}$$

Appendix B shows an equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

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

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for a, b, and c yields:

$$\begin{aligned} x &= \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)} \\ &= \frac{-0.0211 \pm \sqrt{\left(4.45 \times 10^{-4}\right) + \left(8.44 \times 10^{-2}\right)}}{2} \\ &= \frac{-0.0211 \pm 0.291}{2} \end{aligned}$$

The two roots of the quadratic are, therefore,

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

and

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

For this scenario, only the positive root is physically meaningful (concentrations are either zero or positive), and so $x = 0.135$ *M*.

The equilibrium concentrations are

$$[PCl_5] = 1.00 - 0.135 = 0.87\ M$$
$$[PCl_3] = x = 0.135\ M =$$
$$[Cl_2] = x = 0.135\ M$$

Step 4.

Confirm the calculated equilibrium concentrations.

Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures).

Exercise 13.5.4A

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations for a mixture that is initially 0.15 *M* in CH_3CO_2H, 0.15 *M* in C_2H_5OH, 0.40 *M* in $CH_3CO_2C_2H_5$, and 0.40 *M* in H_2O?

Answer

$[CH_3CO_2H]$ = 0.18 *M*, $[C_2H_5OH]$ = 0.18 *M*, $[CH_3CO_2C_2H_5]$ = 0.37 *M*, $[H_2O]$ = 0.37 *M*

Exercise 13.5.4B

A 1.00-L flask is filled with 1.00 mole of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

Answer

$[H_2]$ = 0.06 *M*, $[I_2]$ = 1.06 *M*, [HI] = 1.88 *M*

Example 13.5.5: Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption

What are the concentrations at equilibrium of a 0.15 *M* solution of HCN?

$$HCN\,(aq) \rightleftharpoons H^+\,(aq) + CN^-\,(aq) \qquad K_c = 4.9 \times 10^{-10}$$

Solution

Using "*x*" to represent the concentration of each product at equilibrium gives this ICE table.

	$HCN(aq) \rightleftharpoons$	$H^+(aq)$ +	$CN^-(aq)$
Initial concentration (*M*)	0.15	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.15 - x$	x	x

Substitute the equilibrium concentration terms into the K_c expression

$$K_c = \frac{(x)(x)}{0.15 - x}$$

rearrange to the quadratic form and solve for x

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$
$$x = 8.56 \times 10^{-6} M (3 \text{ sig. figs. }) = 8.6 \times 10^{-6} M (2 \text{ sig. figs. })$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6}$ M and $[HCN] = 0.15 – x = 0.15$ M.

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small K), and so the initial concentration experiences a negligible change:

$$\text{if } x \ll 0.15M, \text{ then } (0.15 - x) \approx 0.15$$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$
$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$
$$x^2 = (0.15)\left(4.9 \times 10^{-10}\right)$$
$$= 7.4 \times 10^{-11}$$
$$x = \sqrt{7.4 \times 10^{-11}}$$
$$= 8.6 \times 10^{-6} \text{ M}$$

The value of x calculated is, indeed, much less than the initial concentration

$$8.6 \times 10^{-6} \ll 0.15$$

and so the approximation was justified. If this simplified approach were to yield a value for x that did *not* justify the approximation, the calculation would need to be repeated without making the approximation.

? Exercise 13.5.5

What are the equilibrium concentrations in a 0.25 M NH_3 solution?

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \quad K_c = 1.8 \times 10^{-5}$$

Answer

$[OH^-] = [NH_4^+] = 0.0021$ M

$[NH_3] = 0.25$ M

This page titled 13.5: Equilibrium Calculations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **13.4: Equilibrium Calculations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

13.6: Key Terms

equilibrium | state of a reversible reaction in which the forward and reverse processes occur at equal rates

equilibrium constant (*K*) | value of the reaction quotient for a system at equilibrium; may be expressed using concentrations (K_c) or partial pressures (K_p)

heterogeneous equilibria | equilibria in which reactants and products occupy two or more different phases

homogeneous equilibria | equilibria in which all reactants and products occupy the same phase

law of mass action | when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Le Chatelier's principle | an equilibrium subjected to stress will shift in a way to counter the stress and re-establish equilibrium

reaction quotient (*Q*) | mathematical function describing the relative amounts of reactants and products in a reaction mixture; may be expressed in terms of concentrations (Q_c) or pressures (Q_p)

reversible reaction | chemical reaction that can proceed in both the forward and reverse directions under given conditions

13.6: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **13.5: Key Terms** is licensed CC BY 4.0.

13.7: Key Equations

$P = MRT$
$K_c = Q_c$ at equilibrium
$K_p = Q_p$ at equilibrium
$K_P = K_c\,(RT)^{\Delta n}$

13.7: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **13.6: Key Equations** is licensed CC BY 4.0.

13.8: Summary

A reversible reaction is at equilibrium when the forward and reverse processes occur at equal rates. Chemical equilibria are dynamic processes characterized by constant amounts of reactant and product species.

The composition of a reaction mixture may be represented by a mathematical function known as the reaction quotient, Q. For a reaction at equilibrium, the composition is constant, and Q is called the equilibrium constant, K.

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure. The system's response to these disturbances is described by Le Chatelier's principle: An equilibrium system subjected to a disturbance will shift in a way that counters the disturbance and re-establishes equilibrium. A catalyst will increase the rate of both the forward and reverse reactions of a reversible process, increasing the rate at which equilibrium is reached but not altering the equilibrium mixture's composition (K does not change).

Calculating values for equilibrium constants and/or equilibrium concentrations is of practical benefit to many applications. A mathematical strategy that uses initial concentrations, changes in concentrations, and equilibrium concentrations (and goes by the acronym ICE) is useful for several types of equilibrium calculations.

13.8: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **13.7: Summary** is licensed CC BY 4.0.

13.9: Exercises

1.

What does it mean to describe a reaction as “reversible”?

2.

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

3.

If a reaction is reversible, when can it be said to have reached equilibrium?

4.

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

5.

If the concentrations of products and reactants are equal, is the system at equilibrium?

6.

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

7.

Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown in Figure 13.4.

8.

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

9.

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

a. Write the expression for the equilibrium constant for the reaction represented by the equation Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
b. Write the expression for the equilibrium constant for the reaction represented by the equation Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

10.

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
b. Write the expression for the equilibrium constant for the reaction represented by the equation Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

11.

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

12.

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and

13.

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

14.

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

15.

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a.
b.
c.
d.
e.
f.
g.
h.

16.

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a.
b.
c.
d.
e.
f.
g.
h.

17.

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. (f) NO = 10.0 atm, $N_2 = O_2 = 5$ atm

18.

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. (f) $[N_2] = 0.100\ M$, $[O_2] = 0.200\ M$, $[NO] = 1.00\ M$

19.

The following reaction has $K_P = 4.50 \times 10^{-5}$ DELMAR at 720 K.

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3) = 93$ atm, $P(N_2) = 48$ atm, and $P(H_2) = 52$ atm

20.

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

$[SO_2Cl_2] = 0.12\ M$, $[Cl_2] = 0.16\ M$ and $[SO_2] = 0.050\ M$. K_c for the reaction is 0.078.

21.

Which of the systems described in Exercise 13.15 are homogeneous equilibria? Which are heterogeneous equilibria?

22.

Which of the systems described in Exercise 13.16 are homogeneous equilibria? Which are heterogeneous equilibria?

23.

For which of the reactions in Exercise 13.15 does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

24.

For which of the reactions in Exercise 13.16 does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

25.

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a.

b.

c.

d.

26.

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a.

b.

c.

d.

27.

What is the value of the equilibrium constant expression for the change

28.

Write the expression of the reaction quotient for the ionization of HOCN in water.

29.

Write the reaction quotient expression for the ionization of NH_3 in water.

30.

What is the approximate value of the equilibrium constant K_P for the change at 25 °C. (The equilibrium vapor pressure for this substance is 570 torr at 25 °C.)

31.

The following equation represents a reversible decomposition:

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

32.

Explain how to recognize the conditions under which changes in volume will affect gas-phase systems at equilibrium.

33.

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

34.

The following reaction occurs when a burner on a gas stove is lit:

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

35.

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

a. Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

b. Is the reaction endothermic or exothermic?

36.

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

37.

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

38.

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a.
b.
c.
d.

39.

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a.
b.
c.
d.

40.

Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

(b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

(c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

(f) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

41.

Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?

(g) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

42.

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

43.

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

44.

Ammonia is a weak base that reacts with water according to this equation:

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

a. Addition of NaOH
b. Addition of HCl
c. Addition of NH_4Cl

45.

Acetic acid is a weak acid that reacts with water according to this equation:

Will any of the following increase the percent of acetic acid that reacts and produces ion?

a. Addition of HCl
b. Addition of NaOH
c. Addition of $NaCH_3CO_2$

46.

Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and in contact with solid AgCl.

47.

How can the pressure of water vapor be increased in the following equilibrium?

48.

A solution is saturated with silver sulfate and contains excess solid silver sulfate:

A small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive Ag^+ ions. Explain this observation.

49.

When equal molar amounts of HCl and HOCl are dissolved separately in equal amounts of water, the solution of HCl freezes at a lower temperature. Which compound has the larger equilibrium constant for acid ionization?

a. HCl

b. $H^+ + Cl^-$
c. HOCl
d. $H^+ + OCl^-$

50.

A reaction is represented by this equation:

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations ≤1 *M*, identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

51.

A reaction is represented by this equation:

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations of ≤1 *M*, identify two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

52.

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12 \times 10^{−1} DELMAR *M* NH_3.

53.

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

54.

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

55.

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 0.0033% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

56.

Calculate the value of the equilibrium constant K_P for the reaction from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

57.

When heated, iodine vapor dissociates according to this equation:

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

58.

A sample of ammonium chloride was heated in a closed container.

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

59.

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the vaporization equilibrium at 60 °C?

60.

Complete the following partial ICE tables.

(a)

(b)

(c)

(d)

(e)

(f)

61.

Complete the following partial ICE tables.

(a)

(b)

(c)

(d)

(e)

(f)

62.

Why are there no changes specified for Ni in Exercise 13.60, part (f)? What property of Ni does change?

63.

Why are there no changes specified for NH_4HS in Exercise 13.61, part (e)? What property of NH_4HS does change?

64.

Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

Calculate the equilibrium molar concentration of NH_3.

65.

Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

66.

What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

67.

What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

68.

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100$ *M*?

69.

Carbon reacts with water vapor at elevated temperatures.

Assuming a reaction mixture initially contains only reactants, what is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500$ *M* at 1000 °C?

70.

Sodium sulfate 10−hydrate, $Na_2SO_4 \cdot 10H_2O$, dehydrates according to the equation

What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4 \cdot 10H_2O$ and $NaSO_4$?

71.

Calcium chloride 6−hydrate, $CaCl_2 \cdot 6H_2O$, dehydrates according to the equation

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2 \cdot 6H_2O$ and $CaCl_2$ at 25 °C?

72.

A student solved the following problem and found the equilibrium concentrations to be $[SO_2]$ = 0.590 *M*, $[O_2]$ = 0.0450 *M*, and $[SO_3]$ = 0.260 *M*. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

73.

A student solved the following problem and found $[N_2O_4]$ = 0.16 *M* at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?

74.

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

in chloroform

(b) Confirm that the change is small enough to be neglected.

75.

Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.

(b) Confirm that the change is small enough to be neglected.

76.

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

(b) Confirm that the change is small enough to be neglected.

77.

What are all concentrations after a mixture that contains $[H_2O]$ = 1.00 *M* and $[Cl_2O]$ = 1.00 *M* comes to equilibrium at 25 °C?

78.

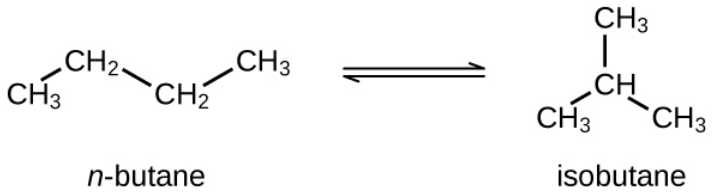
What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5]$ = 2.00 *M*?

79.

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

80.

Butane exists as two isomers, *n*−butane and isobutane.



n-butane isobutane

K_P = 2.5 at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

81.

What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.50 for the decomposition reaction of $CaCO_3$ at that temperature?

82.

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

83.

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00 \times 10^{3} DELMAR torr.

a. How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
b. Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

84.

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

a. On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?
b. Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

85.

Antimony pentachloride decomposes according to this equation:

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

86.

Consider the equilibrium

a. What is the expression for the equilibrium constant (K_c) of the reaction?
b. How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
c. If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of NO_2?
d. If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

87.

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

a. Write the equilibrium constant expression for this reaction.
b. Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

88.

Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of K_P = 1.91 has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

89.

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*? The equilibrium reaction is

---

This page titled 13.9: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **13.8: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

CHAPTER OVERVIEW

14: Acid-Base Equilibria

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

14.1: Introduction
14.2: Summary
14.3: Exercises
14.4: Brønsted-Lowry Acids and Bases
14.5: pH and pOH
14.6: Relative Strengths of Acids and Bases
14.7: Hydrolysis of Salt Solutions
14.8: Polyprotic Acids
14.9: Buffers
14.10: Acid-Base Titrations
14.11: Key Terms
14.12: Key Equations

This page titled 14: Acid-Base Equilibria is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

14.1: Introduction

Liquid water is essential to life on our planet, and chemistry involving the characteristic ions of water, $\mathbf{H^+}$ and $\mathbf{OH^-}$, is widely encountered in nature and society. As introduced in another chapter of this text, acid-base chemistry involves the transfer of hydrogen ions from donors (acids) to acceptors (bases). These $\mathbf{H^+}$ transfer reactions are reversible, and the equilibria established by acid-base systems are essential aspects of phenomena ranging from sinkhole formation (Figure **14.1.1**) to oxygen transport in the human body. This chapter will further explore acid-base chemistry with an emphasis on the equilibrium aspects of this important reaction class.



Figure **14.1.1**: Sinkholes such as this are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: modification of work by Emil Kehnel)

14.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **14.0: Introduction** is licensed CC BY 4.0.

14.2: 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, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

Concentrations of hydronium and hydroxide ions in aqueous media are often represented as logarithmic pH and pOH values, respectively. At 25 °C, the autoprotolysis equilibrium for water requires the sum of pH and pOH to equal 14 for any aqueous solution. The relative concentrations of hydronium and hydroxide ion in a solution define its status as acidic ($[H_3O^+] > [OH^-]$), basic ($[H_3O^+] < [OH^-]$), or neutral ($[H_3O^+] = [OH^-]$). At 25 °C, a pH < 7 indicates an acidic solution, a pH > 7 a basic solution, and a pH = 7 a neutral solution.

The relative strengths of acids and bases are reflected in the magnitudes of their ionization constants; the stronger the acid or base, the larger its ionization constant. A reciprocal relation exists between the strengths of a conjugate acid-base pair: the stronger the acid, the weaker its conjugate base. Water exerts a leveling effect on dissolved acids or bases, reacting completely to generate its characteristic hydronium and hydroxide ions (the strongest acid and base that may exist in water). The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

The ions composing salts may possess acidic or basic character, ionizing when dissolved in water to yield acidic or basic solutions. Acidic cations are typically the conjugate partners of weak bases, and basic anions are the conjugate partners of weak acids. Many metal ions bond to water molecules when dissolved to yield complex ions that may function as acids.

An acid that contains more than one ionizable proton is a polyprotic acid. These acids undergo stepwise ionization reactions involving the transfer of single protons. The ionization constants for polyprotic acids decrease with each subsequent step; these decreases typically are large enough to permit simple equilibrium calculations that treat each step separately.

Solutions that contain appreciable amounts of a weak conjugate acid-base pair are called buffers. A buffered solution will experience only slight changes in pH when small amounts of acid or base are added. Addition of large amounts of acid or base can exceed the buffer capacity, consuming most of one conjugate partner and preventing further buffering action.

The titration curve for an acid-base titration is typically a plot of pH versus volume of added titrant. These curves are useful in selecting appropriate acid-base indicators that will permit accurate determinations of titration end points.

14.2: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **14.10: Summary** is licensed CC BY 4.0.

14.3: Exercises

1.

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

2.

Write equations that show acting both as an acid and as a base.

3.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. (f)

4.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. (f) HS^-

5.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

a. (f)

6.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

a. (f)

7.

What is the conjugate acid of each of the following? What is the conjugate base of each?

a. OH^-
b. H_2O
c.
d. NH_3
e.
f. H_2O_2
g. HS^-
h.

8.

What is the conjugate acid of each of the following? What is the conjugate base of each?

a. H_2S
b.
c. PH_3
d. HS^-
e.
f.
g. H_4N_2
h. CH_3OH

9.

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. (f)

10.

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. (f)

11.

What are amphiprotic species? Illustrate with suitable equations.

12.

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

a. H_2O
b.
c. S^{2-}
d.
e.

13.

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

a. NH_3
b.
c. Br^-
d.
e.

14.

Is the self-ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9 \times 10^{−14} at 40 °C and 9.3 \times 10^{−14} at 60 °C.

15.

Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+]$ = 1.7 \times 10^{−7} *M*. K_w is 2.9 \times 10^{−14} at 40 °C.

16.

The ionization constant for water (K_w) is 2.9 \times 10^{−14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

17.

The ionization constant for water (K_w) is 9.311 \times 10^{−14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

18.

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.200 *M* HCl
b. 0.0143 *M* NaOH
c. 3.0 *M* HNO_3
d. 0.0031 *M* $Ca(OH)_2$

19.

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.000259 *M* $HClO_4$
b. 0.21 *M* NaOH

c. 0.000071 *M* $Ba(OH)_2$
d. 2.5 *M* KOH

20.

What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

21.

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

22.

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 14.2 for useful information.

23.

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 14.2 for useful information.

24.

The hydronium ion concentration in a sample of rainwater is found to be 1.7 \times 10^{−6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?

25.

The hydroxide ion concentration in household ammonia is 3.2 \times 10^{−3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?

26.

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

27.

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

28.

Use this list of important industrial compounds (and Figure 14.8) to answer the following questions regarding: $Ca(OH)_2$, CH_3CO_2H, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

a. Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
b. Identify the compounds that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
c. Identify the compounds that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

29.

The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

30.

Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

31.

Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

32.

Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

33.

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

34.

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

35.

What is the ionization constant at 25 °C for the weak acid the conjugate acid of the weak base CH_3NH_2, K_b = 4.4 \times 10^{−4}.

36.

What is the ionization constant at 25 °C for the weak acid the conjugate acid of the weak base $(CH_3)_2NH$, K_b = 5.9 \times 10^{−4}?

37.

Which base, CH_3NH_2 or $(CH_3)_2NH$, is the stronger base? Which conjugate acid, or , is the stronger acid?

38.

Which is the stronger acid, or HBrO?

39.

Which is the stronger base, $(CH_3)_3N$ or

40.

Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

a. H_2O or HF
b. $B(OH)_3$ or $Al(OH)_3$
c. or
d. NH_3 or H_2S
e. H_2O or H_2Te

41.

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

a. or
b. NH_3 or H_2O
c. PH_3 or HI
d. NH_3 or PH_3
e. H_2S or HBr

42.

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. acidity: HCl, HBr, HI
b. basicity: H_2O, OH^-, H^-, Cl^-
c. basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$.)
d. acidity: HF, H_2O, NH_3, CH_4

43.

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. (f) basicity: BrO^-,

44.

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base?

45.

The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

46.

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

47.

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid or base?

48.

Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water?

a. addition of NaOH
b. addition of HCl
c. addition of NH_4Cl

49.

Which of the following will increase the percentage of HF that is converted to the fluoride ion in water?

a. addition of NaOH
b. addition of HCl
c. addition of NaF

50.

What is the effect on the concentrations of HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

a. HCl
b. HNO_2
c. NaOH
d. NaCl
e. KNO

51.

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

a. HCl
b. KF
c. NaCl
d. KOH
e. HF

52.

Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

53.

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) CH_3CO_2H: = 1.34 \times 10^{−3} *M*;
= 1.34 \times 10^{−3} *M*;

$[CH_3CO_2H]$ = 9.866 \times 10^{−2} *M*;

(b) ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*;

$[HClO] = 2.38 \times 10^{-4}$ *M*;

$[ClO^-] = 0.273$ *M*;

(c) HCO_2H: $[HCO_2H] = 0.524$ *M*;
$= 9.8 \times 10^{-3}$ *M*;
$= 9.8 \times 10^{-3}$ *M*;

(d) = 0.233 *M*;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;
$= 2.3 \times 10^{-3}$ *M*

54.

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;
$= 3.1 \times 10^{-3}$ *M*;

$[NH_3] = 0.533$ *M*;

(b) HNO_2: = 0.011 *M*;
= 0.0438 *M*;

$[HNO_2] = 1.07$ *M*;

(c) $(CH_3)_3N$: $[(CH_3)_3N] = 0.25$ *M*;
$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}$ *M*;

$[OH^-] = 3.7 \times 10^{-3}$ *M*;

(d) = 0.100 *M*;

$[NH_3] = 7.5 \times 10^{-6}$ *M*;
$[H_3O^+] = 7.5 \times 10^{-6}$ *M*

55.

Determine K_b for the nitrite ion, In a 0.10-*M* solution this base is 0.0015% ionized.

56.

Determine K_a for hydrogen sulfate ion, In a 0.10-*M* solution the acid is 29% ionized.

57.

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

a. (f) (as a base)

58.

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

a. (f) (as a base)

59.

Using the K_a value of 1.4

60.

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.

a. 0.0092 *M* HClO, a weak acid
b. 0.0784 *M* $C_6H_5NH_2$, a weak base
c. 0.0810 *M* HCN, a weak acid
d. 0.11 *M* $(CH_3)_3N$, a weak base
e. 0.120 *M* a weak acid, $K_a = 1.6 \times 10^{-7}$

61.

Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-*M* solution of $C_2H_5CO_2H$?

62.

White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

63.

The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

64.

Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_{b1} = 7 \times 10^{-7}$, $K_{b2} = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

65.

The pH of a 0.23-*M* solution of HF is 1.92. Determine K_a for HF from these data.

66.

The pH of a 0.15-*M* solution of is 1.43. Determine K_a for from these data.

67.

The pH of a 0.10-*M* solution of caffeine is 11.70. Determine K_b for caffeine from these data:

68.

The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

69.

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $Al(NO_3)_3$
b. RbI
c. $KHCO_2$
d. CH_3NH_3Br

70.

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $FeCl_3$
b. K_2CO_3
c. NH_4Br
d. $KClO_4$

71.

Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

72.

Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid: [OH^-], [H_2CO_3], No calculations are needed to answer this question.

73.

Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

74.

Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

75.

Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

a. Both functional groups of salicylic acid ionize in water, with K_a = 1.0 \times 10^{−3} for the—CO_2H group and 4.2 \times 10^{−13} for the −OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).
b. Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, K_a = 3.0 \times 10^{−4}. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

76.

The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

a. What is K_a for the acid reaction of HTe^- with H_2O?
b. What is K_b for the reaction in which HTe^- functions as a base in water?
c. Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of [HTe^-] in a 0.10 M solution of H_2Te.

77.

Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

78.

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

79.

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

80.

What is [H_3O^+] in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

81.

What is [H_3O^+] in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

82.

What is [OH^-] in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

83.

What is [OH^-] in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

84.

What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

a. HCl

b. KCH_3CO_2
c. NaCl
d. KOH
e. CH_3CO_2H

85.

What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

a. KI
b. NH_3
c. HI
d. NaOH
e. NH_4Cl

86.

What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

87.

Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

88.

How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

89.

What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

90.

A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80 \times 10^{−5} as K_a for acetic acid.

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 0.034 *M* HCl is added to 0.200 L of the original buffer?

91.

A 5.36–g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution

diluted to 0.100 L.

a. What is the pH of this buffer solution?
b. Is the solution acidic or basic?
c. What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

92.

Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

93.

Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

94.

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid (K_a = 9.8 \times 10^{−5}) with 0.100 *M* KOH.

a. no KOH added
b. 20 mL of KOH solution added
c. 39 mL of KOH solution added
d. 40 mL of KOH solution added
e. 41 mL of KOH solution added

95.

The indicator dinitrophenol is an acid with a K_a of 1.1 \times 10^{−4}. In a 1.0 \times 10^{−4}-*M* solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

This page titled 14.3: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.11: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14.4: Brønsted-Lowry Acids and Bases

Learning Objectives

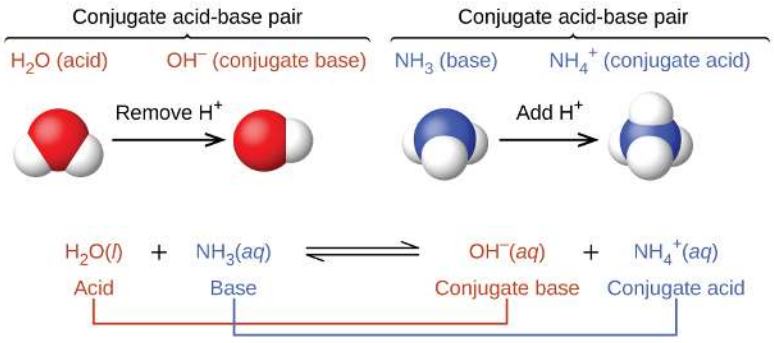
By the end of this section, you will be able to:

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

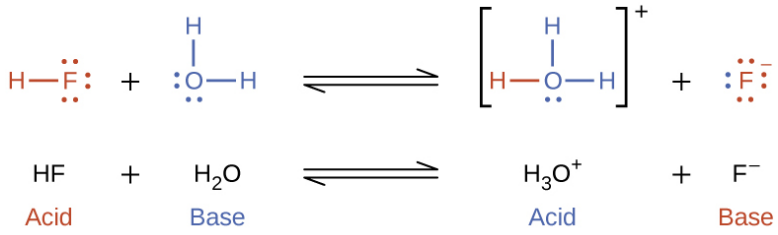
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H.) A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

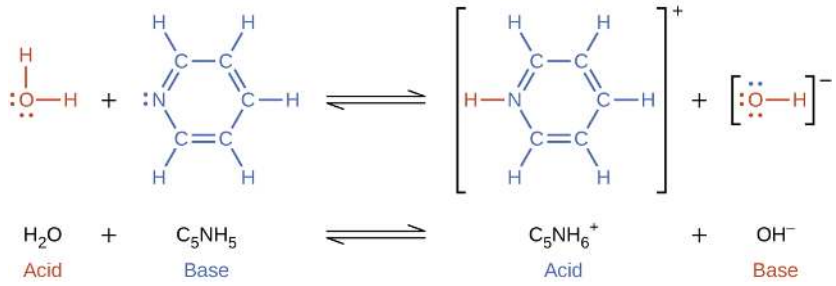
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts H^+, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, OH^-, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, NH_4^+, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.



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:



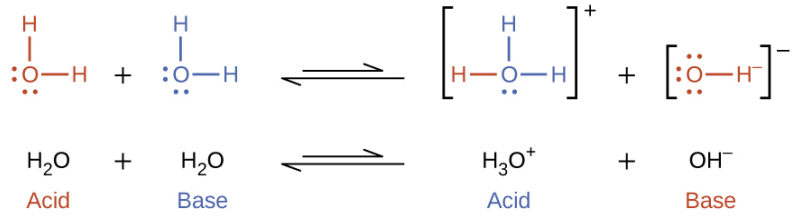
The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called amphiprotic, or more generally, amphoteric, a term that may be used for acids and bases per definitions other than the Brønsted-Lowry one. The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations, as described later in this chapter.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below:



The process in which like molecules react to yield ions is called autoionization. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the ion-product constant for water, K_w:

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{14.4.1}$$

with

$$K_w = [H_3O^+][OH^-] \tag{14.4.2}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and

hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 14.4.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-] = x$. 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 14.4.1

The ion product of water at 80 °C is 2.4 \times 10^{−13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\,M$$

Example 14.4.2: The Inverse Relation between $[H_3O^+]$ and $[OH^-]$

A solution of an acid in water has a hydronium ion concentration of $2.0 \times 10^{-6} M$. What is the concentration of hydroxide ion at 25 °C?

Solution

Use the value of the ion-product constant for water at 25 °C (Equations 14.4.1 and 14.4.2) to calculate the missing equilibrium concentration.

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

with $K_w = [H_3O^+][OH^-]$.

Rearrangement of the K_w expression shows that $[OH^-]$ is inversely proportional to $[H_3O^+]$:

$$K_w = [H_3O^+]\,[OH^-] = (2.0 \times 10^{-6})\,(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Chatelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the K_w expression confirms this calculation, resulting in the expected value:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 14.4.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 *M* at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11}\ M$$

Example 14.4.3: Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

Exercise 14.4.3

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer

a. $H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$
b. $H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$

This page titled 14.4: Brønsted-Lowry Acids and Bases is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.1: Brønsted-Lowry Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14.5: pH and pOH

Learning Objectives

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

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$pX = -\log X$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$pH = -\log [H_3O^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[H_3O^+] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$pOH = -\log [OH^-]$$

or

$$[OH^-] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_w &= [\mathrm{H_3O^+}]\,[\mathrm{OH^-}] \\ -\log K_w &= -\log \left([\mathrm{H_3O^+}]\,[\mathrm{OH^-}]\right) \\ &= -\log [\mathrm{H_3O^+}] + -\log [\mathrm{OH^-}] \\ pK_w &= pH + pOH \end{aligned} \tag{14.5.1}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = pH + pOH$$

As was demonstrated previously, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} M at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log [H_3O^+] = -\log \left(1.0 \times 10^{-7}\right) = 7.00$$

$$pOH = -\log [OH^-] = -\log \left(1.0 \times 10^{-7}\right) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} M and hydroxide ion molarities less than 1.0×10^{-7} M (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are

those with hydronium ion molarities less than 1.0×10^{-7} M and hydroxide ion molarities greater than 1.0×10^{-7} M (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, Exercise **14.5.1** showed the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} M, which corresponds to pH and pOH values of:

$$pH = -\log\left[H_3O^+\right] = -\log\left(4.9 \times 10^{-7}\right) = 6.31$$

$$pOH = -\log\left[OH^-\right] = -\log\left(4.9 \times 10^{-7}\right) = 6.31$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C. Unless otherwise noted, references to pH values are presumed to be those at 25 °C (Table **14.5.1**).

Table **14.5.1**: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure **14.5.1**: shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

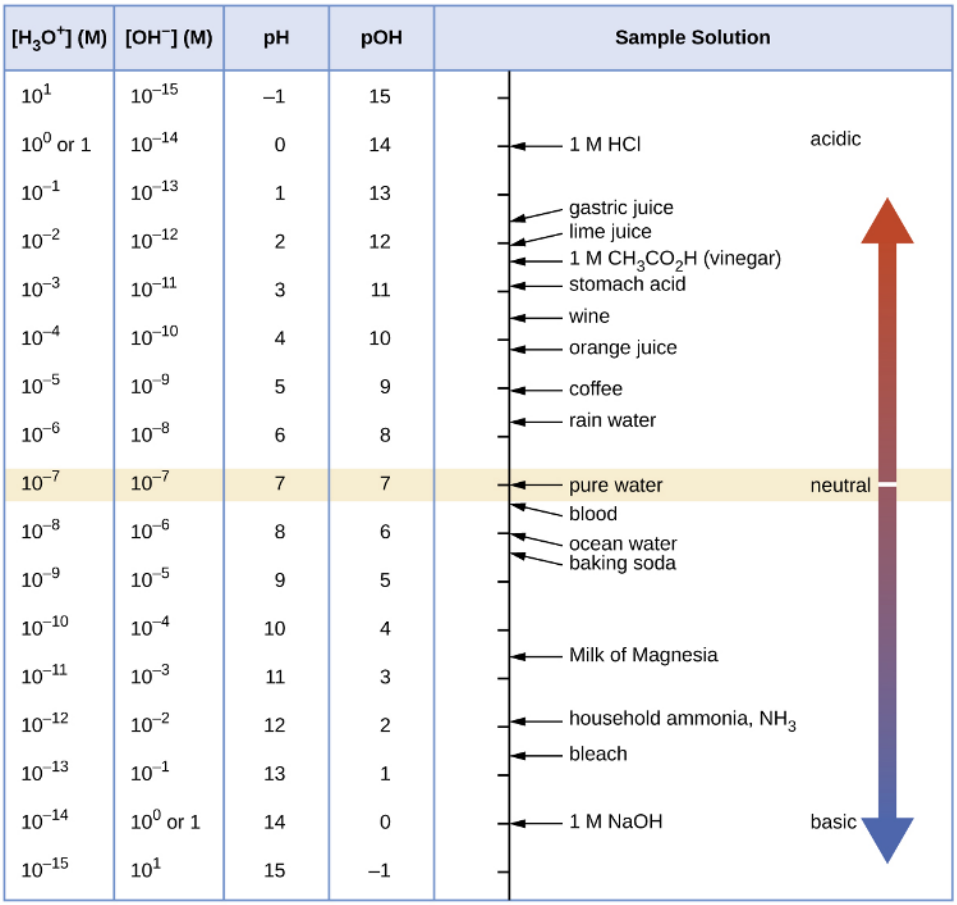


Figure **14.5.1**: The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

Example 14.5.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log\left[H_3O^+\right] \\ &= -\log\left(1.2 \times 10^{-3}\right) \\ &= -(-2.92) = 2.92 \end{aligned}$$

(The use of logarithms is explained in Appendix B. When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Exercise 14.5.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of 2.0×10^{-6} M, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 14.5.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned} pH = -\log\left[H_3O^+\right] &= 7.3 \\ \log\left[H_3O^+\right] &= -7.3 \\ \left[H_3O^+\right] &= 10^{-7.3} \end{aligned}$$

or

$$\begin{aligned} \left[H_3O^+\right] &= \text{antilog of } -7.3 \\ &= 5 \times 10^{-8} M \end{aligned}$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 14.5.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 *M*

How Sciences Interconnect: Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)$$
$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure **14.5.2**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this website hosted by the US Environmental Protection Agency.



(a) (b)

Figure **14.5.2**: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

✔ Example ✔ 14.5.3: Calculation of pOH

What are the **pOH** and the \(\text{pH} of a 0.0125-*M* solution of potassium hydroxide, **KOH**?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-]$ = 0.0125 *M*:

$$\text{pOH} = -\log[OH^-] = -\log 0.0125$$
$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$
$$pH = 14.00 - pOH$$
$$= 14.00 - 1.903 = 12.10$$

? Exercise 14.5.3

The hydronium ion concentration of vinegar is approximately 4×10^{-3} M. What are the corresponding values of **pOH** and **pH**?

Answer

pOH = 11.6, pH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure **14.5.3**).



(a) (b)

Figure **14.5.3**: (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 may also be visually estimated using colored indicators (Figure **14.5.4**). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.



(a) (b)

Figure **14.5.4**: (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)

This page titled 14.5: pH and pOH is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.2: pH and pOH** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

https://chem.libretexts.org/@go/page/548577

14.6: Relative Strengths of Acids and Bases

Learning Objectives

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

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

Acid and Base Ionization Constants

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in Figure **14.6.1**.

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 **14.6.1**: Some of the common strong acids and bases are listed here.

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid **HA**:

$$\mathbf{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)}$$

the acid ionization constant is written

$$K_a = \frac{[\mathbf{H_3O^+}][\mathbf{A^-}]}{[\mathbf{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[\mathbf{H_2O}]$ in the equation.

Note

Equilibrium constant expressions are actually ratios of activities, and the value of K is determined at the limit of infinite dilution of the solutes. In these very dilute solutions, the activity of the solvent has a value of unity (1) and the activity of each solute can be approximated by its molar concentration.

The larger the K_a of an acid, the larger the concentration of $\mathbf{H_3O^+}$ and $\mathbf{A^-}$ relative to the concentration of the nonionized acid, **HA**, in an equilibrium mixture, and the stronger the acid. An acid is classified as “strong” when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called “weak,” and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in Appendix H.

To illustrate this idea, three acid ionization equations and K_a values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order:

$$\ce{CH3CO2H} < \ce{HNO2} < \ce{HSO4^-}$$

as demonstrated with the equations below:

$$\ce{CH3CO2H(aq) + H2O(l) <=> H3O^+(aq) + CH3CO2^-(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

$$\ce{HNO2(aq) + H2O(l) <=> H3O^+(aq) + NO2^-(aq)} \qquad K_a = 4.6 \times 10^{-4}$$

$$\ce{HSO4^-(aq) + H2O(aq) <=> H3O^+(aq) + SO4^2-(aq)} \qquad K_a = 1.2 \times 10^{-2}$$

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:

$$\%\ \text{ionization} = \frac{[\ce{H3O^+}]_{eq}}{[\ce{HA}]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$). 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 14.6.1: 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:

$$\frac{[\ce{H3O^+}]_{eq}}{[\ce{HNO2}]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[\ce{H3O^+}] = 10^{-2.09} = 0.0081M$$

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 14.6.1

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

Link to Learning

View the simulation of strong and weak acids and bases at the molecular level.

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. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, **B**:

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons HB^+\,(aq) + OH^-\,(aq)},$$

the ionization constant is written as

$$K_b = \frac{[\mathrm{HB^+}]\,[\mathrm{OH^-}]}{[\mathrm{B}]}$$

Inspection of the data for three weak bases presented below shows the base strength increases in the order: $\mathrm{NO_2^-} < \mathrm{CH_2CO_2^-} < \mathrm{NH_3}$

$$\mathrm{NO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HNO_2\,(aq) + OH^-\,(aq)} \qquad K_b = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3\,CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3\,CO_2\,H\,(aq) + OH^-\,(aq)} \qquad K_b = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \qquad K_b = 1.8 \times 10^{-5}$$

A table of ionization constants for weak bases appears in Appendix I. 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.

Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b, which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair $\mathrm{HA\ /\ A^-}$, ionization equilibrium equations and ionization constant expressions are

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)}$$

with

$$K_a = \frac{[H3O^+][A^-]}{[HA]}$$

and

$$\mathrm{A^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + HA\,(aq)}$$

with

$$K_b = \frac{[HA][OH-]}{[A-]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{HA(aq)} + \mathrm{H_2O\,(l)} + \cancel{A^-(aq)} + \mathrm{H_2O\,(l) \rightleftharpoons H_3O^+\,(aq)} + \cancel{A^-(aq)} + \mathrm{OH^-\,(aq)} + \cancel{HA(aq)}$$
$$\mathrm{2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)}$$

As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$K_a \times K_b = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w. By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_a = \frac{K_w}{K_b}$$

or

$$K_b = \frac{K_w}{K_a}$$

The inverse proportional relation between K_a and K_b means the stronger the acid or base, the weaker its **conjugate partner**. Figure **14.6.2**: illustrates this relation for several conjugate acid-base pairs.

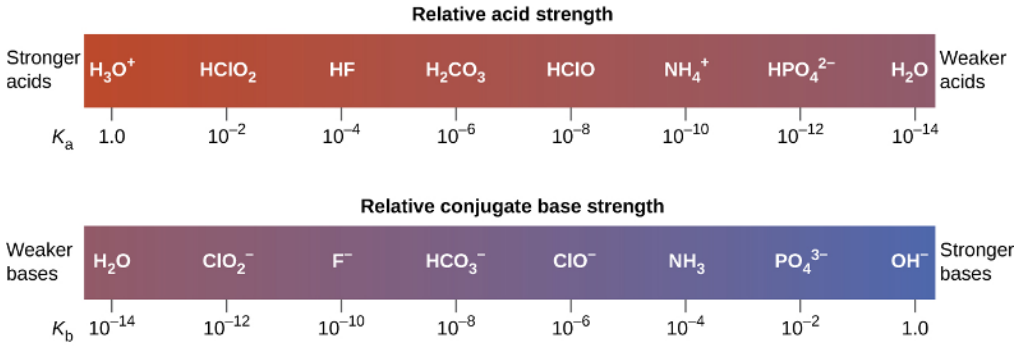


Figure **14.6.2**: Relative strengths of several conjugate acid-base pairs are shown.

The listing of conjugate acid–base pairs shown in Figure **14.6.3**: is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table's columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, wheres those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

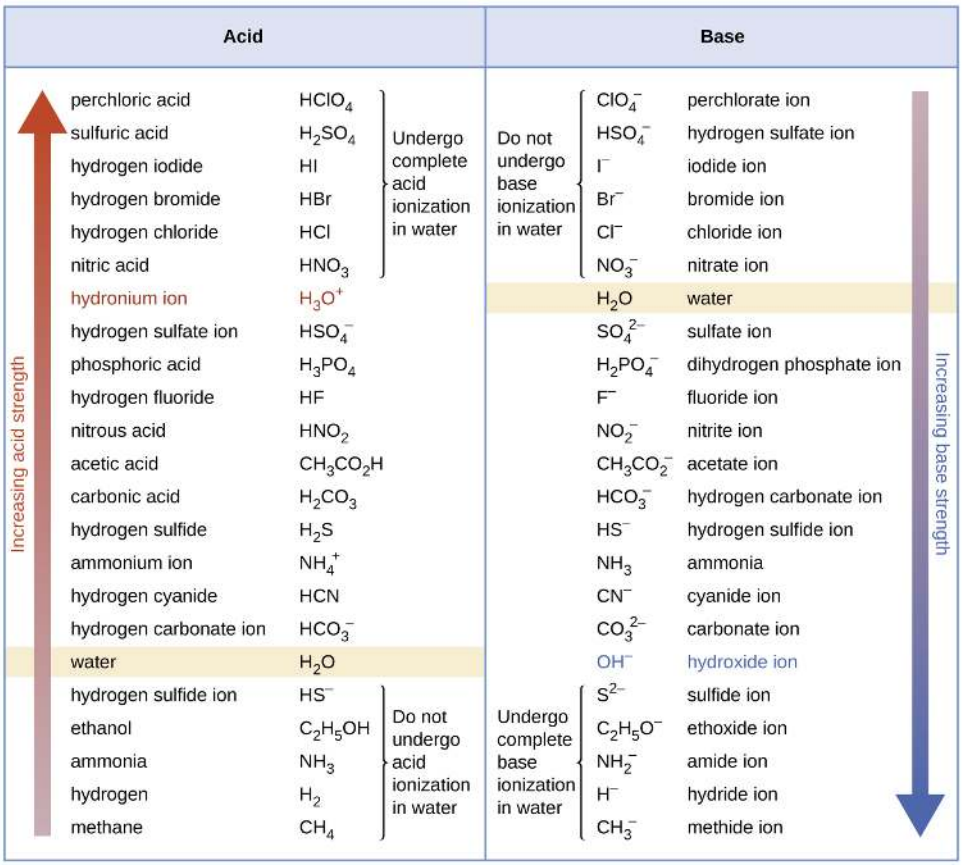


Figure **14.6.3**: This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole acid species present in an aqueous solution of any strong acid is $H_3O^+(aq)$, meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for "strong" acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be "weak," and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are strong acids in water but weak acids in ethanol (strength increasing HCl < HBr < HI).

The right column of Figure **14.6.3** lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don't undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large K_a, and so its conjugate base will exhibit a K_b that is essentially zero:

- strong acid: $K_a \approx \infty$
- conjugate base: $K_b = K_w/K_a = K_w/\infty \approx 0$

A similar approach can be used to support the observation that conjugate acids of strong bases ($K_b \approx \infty$) are of negligible strength ($K_a \approx 0$).

Example 14.6.2: Calculating Ionization Constants for Conjugate Acid-Base Pairs

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a yields

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the Ka for HNO_2 in Appendix H.

Exercise 14.6.2

Determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Appendix H as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}.

Answer

NH_4^+ is the slightly stronger acid (K_a for NH_4^+ is 5.6×10^{-10}).

Acid-Base Equilibrium Calculations

The chapter on chemical equilibria introduced several types of equilibrium calculations and the various mathematical strategies that are helpful in performing them. These strategies are generally useful for equilibrium systems regardless of chemical reaction class, and so they may be effectively applied to acid-base equilibrium problems. This section presents several example exercises involving equilibrium calculations for acid-base systems.



Litmus paper in action

Example 14.6.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 14.6.4) that provides its sour taste. At equilibrium, a solution contains $[CH_3CO_2H] = 0.0787\ M$: and $H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Figure **14.6.4**: Vinegar contains acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the Ka for acetic acid.

$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2{}^-\,(aq)}$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{CH_3CO_2{}^-}]}{[\mathrm{CH_3CO_2H}]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

? Exercise 14.6.3

The $\mathrm{HSO_4{}^-}$ ion, weak acid used in some household cleansers:

$$\mathrm{HSO_4{}^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + SO_4{}^{2-}\,(aq)}$$

What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition: $[\mathrm{H_3O^+}] = 0.027\ M$; $[\mathrm{HSO_4{}^-}] = 0.29\ M$; $[\mathrm{HSO_4{}^-}] = 0.29\ M$; and $[\mathrm{SO_4{}^{2-}}] = 0.13\ M$?

Answer

K_a for $\mathrm{HSO_4{}^-} = 1.2 \times 10^{-2}$

✓ Example 14.6.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $\mathrm{C_8H_{10}N_4O_2}$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[\mathrm{C_8H_{10}N_4O_2}] = 0.050\ \mathrm{M}$, $[\mathrm{C_8H_{10}N_4O_2H^+}] = 5.0 \times 10^{-3}\ \mathrm{M}$, and $[\mathrm{OH^-}] = 2.5 \times 10^{-3}\ \mathrm{M}$?

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_b for caffeine.

$$\mathrm{C_8H_{10}N_4O_2\,(aq) + H_2O\,(l) \rightleftharpoons C_8H_{10}N_4O_2H^+\,(aq) + OH^-\,(aq)}$$

$$\begin{aligned} K_b &= [\mathrm{C_8H_{10}N_4O_2H^+}][\mathrm{OH^-}][\mathrm{C_8H_{10}N_4O_2}] \\ &= (5.0 \times 10^{-3})(2.5 \times 10^{-3})(0.050) \\ &= 2.5 \times 10^{-4} \end{aligned}$$

Exercise 14.6.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^{-}(aq) + OH^{-}(aq)$$

if the composition of an equilibrium mixture is as follows: Extra close brace or missing open brace; $H_2PO_4^{-}] = 0.042\ M$; and $[HPO_4^{2-}] = 0.341\ M$?

Answer

K_b for HPO_4^{2-} is 1.6×10^{-7}

Example 14.6.5: 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 nitrous acid concentration provided is a *formal* concentration, one that does not account for any chemical equilibria that may be established in solution. Such concentrations are treated as "initial" values for equilibrium calculations using the ICE table approach. Notice the initial value of hydronium ion is listed as *approximately* zero because a small concentration of H_3O^+ is present ($1 \times \times 10^{-7}$ M) due to the autoprotolysis of water. In many cases, such as all the ones presented in this chapter, this concentration is much less than that generated by ionization of the acid (or base) in question and may be neglected.

The pH provided is a logarithmic measure of the hydronium ion concentration resulting from the acid ionization of the nitrous acid, and so it represents an "equilibrium" value for the ICE table:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The ICE table for this system is then

	HNO_2	+ H_2O ⇌	H_3O^+	+ 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

Finally, calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+]\,[NO_2^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.6 \times 10^{-4}$$

Exercise 14.6.5

The pH of a solution of household ammonia, a 0.950-M solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$K_b = 1.8 \times 10^{-5}$

Example 14.6.6: Calculating Equilibrium Concentrations in a Weak Acid Solution

Formic acid, HCO_2H, is one irritant that causes the body's reaction to some ant bites and stings (Figure 14.6.5).



Figure **14.6.5**: 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* solution of formic acid?

$$\mathrm{HCO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_2^-\,(aq)} \quad K_a = 1.8 \times 10^{-4}$$

Solution

The ICE table for this system is

	$\mathrm{HCO_2H}$ + $\mathrm{H_2O}$ ⇌	$\mathrm{H_3O^+}$	+ $\mathrm{HCO_2^-}$
Initial concentration (*M*)	0.534	~0	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)	$0.534 - x$	x	x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.8 \times 10^{-4} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{HCO_2^-}]}{[\mathrm{HCO_2H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

The relatively large initial concentration and small equilibrium constant permits the simplifying assumption that x will be much lesser than 0.534, and so the equation becomes

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

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 check the assumption that x is small compared to 0.534, its relative magnitude can be estimated:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} (1.8\% \text{ of } 0.534)$$

Because x is less than 5% of the initial concentration, the assumption is valid.

As defined in the ICE table, x is equal to the equilibrium concentration of hydronium ion:

$$x = [\mathrm{H_3O^+}] = 0.0098 \text{ M}$$

Finally, the pH is calculated to be

$$\text{pH} = -\log\left[\text{H}_3\text{O}^+\right] = -\log(0.0098) = 2.01$$

Exercise 14.6.6

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\text{CH}_3\text{CO}_2\text{H}\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+\,(\text{aq}) + \text{CH}_3\text{CO}_2{}^-\,(\text{aq}) \quad K_a = 1.8 \times 10^{-5}$$

Answer

percent ionization = 1.3%

Example 14.6.7: Calculating Equilibrium Concentrations in a Weak Base Solution

Find the concentration of hydroxide ion, the pOH, and the pH of a 0.25-*M* solution of trimethylamine, a weak base:

$$(\text{CH}_3)_3\text{N}\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l}) \rightleftharpoons (\text{CH}_3)_3\text{NH}^+\,(\text{aq}) + \text{OH}^-\,(\text{aq}) \quad K_b = 6.3 \times 10^{-5}$$

Solution

The ICE table for this system is

	$(CH_3)_3N$ + 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*

Substituting the equilibrium concentration terms into the K_b expression gives

$$K_b = \frac{\left[(\text{CH}_3)_3\text{NH}^+\right]\left[\text{OH}^-\right]}{\left[(\text{CH}_3)_3\text{N}\right]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assuming $x \ll 0.25$ and solving for x yields

$$x = 4.0 \times 10^{-3}\ \text{M}$$

This value is less than 5% of the initial concentration (0.25), so the assumption is justified. As defined in the ICE table, x is equal to the equilibrium concentration of hydroxide ion:

$$\begin{aligned}[OH^-] &=\sim 0 + x \\ &= x = 4.0 \times 10^{-3} M\end{aligned}$$

The pOH is calculated to be

$$\text{pOH} = -\log\left(4.0 \times 10^{-3}\right) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = pK_w = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

Exercise 14.6.7

Calculate the hydroxide ion concentration and the percent ionization of a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Answer

7.56×10^{-4} M, 2.33%

In some cases, the strength of the weak acid or base and its formal (initial) concentration result in an appreciable ionization. Though the ICE strategy remains effective for these systems, the algebra is a bit more involved because the simplifying assumption that *x* is negligible cannot be made. Calculations of this sort are demonstrated in Example **14.6.8** below.

Example 14.6.8: Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, NaHSO4, 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^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

The ICE table for this system is

	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*

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+]\,[SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

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 clearly not significantly less than 0.50 *M*; rather, it is approximately 15% of the initial concentration: When we check the assumption, we calculate:

$$\frac{x}{[HSO_4^-]_i}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

Because the simplifying assumption is not valid for this system, the equilibrium constant expression is solved as follows:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^2$$

Writing the equation in quadratic form gives

$$x^2 + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to *x*. As defined in the ICE table, x is equal to the hydronium concentration.

$$x = [H3O^+] = 0.072\ \text{M}$$

$$\text{pH} = -\log\left[\text{H}_3\text{O}^+\right] = -\log(0.072) = 1.14$$

? Exercise 14.6.8

Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\text{C}_8\text{H10N}_4\text{O}_2\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l}) \rightleftharpoons \text{C}_8\text{H10N}_4\text{O}_2\text{H}^+\,(\text{aq}) + \text{OH}^-\,(\text{aq}) \quad K_b = 2.5 \times 10^{-4}$$

Answer

pH = 11.16

Effect of Molecular Structure on Acid-Base Strength

Binary Acids and Bases

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is

$$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}.$$

Likewise, for group 16, the order of increasing acid strength is

$$\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}\,.$$

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$; across the third row, it is $\text{SiH}_4 < \text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$ (see Figure 14.6.6).

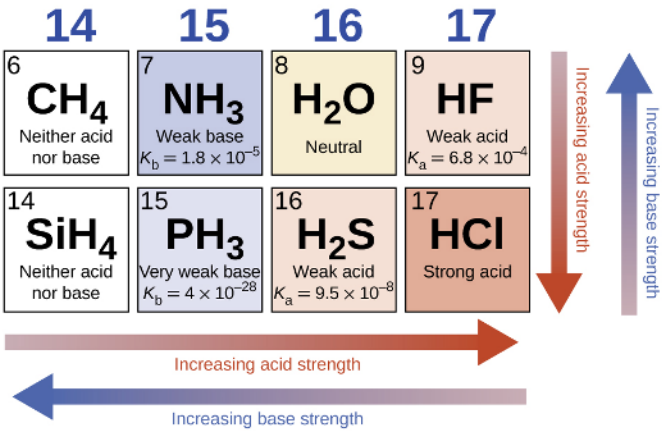
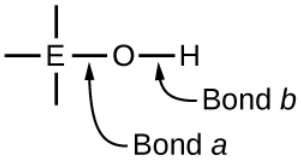


Figure 14.6.6: The figure shows trends in the strengths of binary acids and bases.

Ternary Acids and Bases

Ternary compounds composed of hydrogen, oxygen, and some third element (“E”) may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula $O_mE(OH)_n$. These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure **14.6.7**).

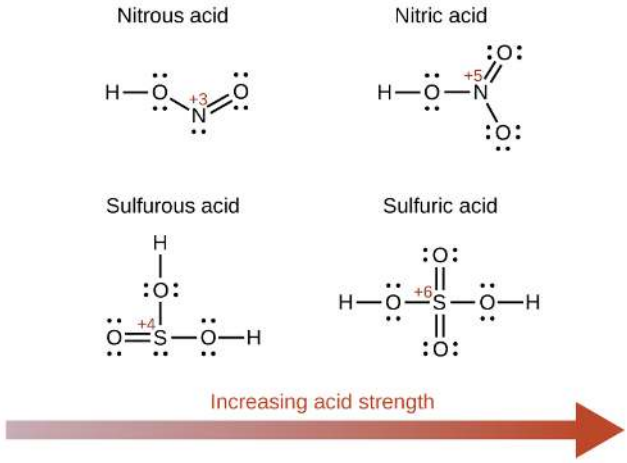


Figure **14.6.7**: As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\mathbf{Al(H_2O)_3(OH)_3}$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\mathbf{Al(H_2O)_3(OH)_3}$, is converted into the soluble ion, $\mathbf{[Al(H_2O)_2(OH)_4]^-}$, by reaction with hydroxide ion:

$$\mathbf{Al(H_2O)_3(OH)_3\,(aq) + OH^-\,(aq) \rightleftharpoons H_2O\,(l) + [Al(H_2O)_2(OH)_4]^-\,(aq)}$$

In this reaction, a proton is transferred from one of the aluminum-bound H2O molecules to a hydroxide ion in solution. The $\mathbf{Al(H_2O)_3(OH)_3}$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $\mathbf{[Al(H_2O)_6]^{3+}}$ by reaction with hydronium ion:

$$\mathbf{3\,H_3O^+\,(aq) + Al(H_2O)_3(OH)_3\,(aq) \rightleftharpoons Al(H_2O)_6^{3+}\,(aq) + 3\,H_2O\,(l)}$$

In this case, protons are transferred from hydronium ions in solution to $\mathbf{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

This page titled 14.6: Relative Strengths of Acids and Bases is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.3: Relative Strengths of Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14.7: Hydrolysis of Salt Solutions

Learning Objectives

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

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation

$$\mathrm{NH_4Cl\,(s) \rightleftharpoons NH_4^+\,(aq) + Cl^-\,(aq)}$$

The ammonium ion is the conjugate acid of the base ammonia, NH_3; its acid ionization (or acid hydrolysis) reaction is represented by

$$\mathrm{NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NH_3\,(aq)} \quad K_a = K_w/K_b$$

Since ammonia is a weak base, K_b is measurable and $K_a > 0$ (ammonium ion is a weak acid).

The chloride ion is the conjugate base of hydrochloric acid, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$\mathrm{Cl^-\,(aq) + H_2O\,(l) \rightleftharpoons HCl\,(aq) + OH^-\,(aq)} \quad K_b = K_w/K_a$$

Since HCl is a strong acid, K_a is immeasurably large and $K_b \approx 0$ (chloride ions don't undergo appreciable hydrolysis).

Thus, dissolving ammonium chloride in water yields a solution of weak acid cations (NH_4^+) and inert anions (Cl^-), resulting in an acidic solution.

Example 14.7.1: Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride, 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

$$\mathrm{C_6H_5NH_3^+\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + C_6H_5NH_2\,(aq)}$$

Solution

The K_a for anilinium ion is derived from the K_b for its conjugate base, aniline (see Appendix H):

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Using the provided information, an ICE table for this system is prepared:

	$C_6H_5NH_3^+$ +	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

Substituting these equilibrium concentration terms into the K_a expression gives

$$K_a = \frac{[C_6H_5NH_2]\,[H_3O^+]}{[C_6H_5NH_3^+]}$$

$$2.3 \times 10^{-5} = \frac{(x)(x)}{0.233 - x}$$

Assuming $x \ll 0.233$, the equation is simplified and solved for x:

$$2.3 \times 10^{-5} = \frac{x^2}{0.233}$$

$$x = 0.0023\ \text{M}$$

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

$$\text{pH} = -\log\,[H_3O^+] = -\log(0.0023) = 2.64$$

? Exercise 14.7.1

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions NH_4^+ and NO_3^- and.

Which is the stronger acid $C_6H_5NH_3^+$ or NH_4^+?

Answer

$[H_3O^+] = 7.5 \times 10^{-6}$ M; is the stronger acid.

Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

$$NaCH_3CO_2\,(s) \rightleftharpoons Na^+\,(aq) + CH_3CO_2^-\,(aq)$$

The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH. This may seem obvious from the ion's formula, which indicates no hydrogen or oxygen atoms, but some dissolved metal ions function as weak acids, as addressed later in this section.

The acetate ion, $CH_3CO_2^-\,(aq)$, is the conjugate base of acetic acid, CH_3CO_2H, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3\ CO_2\ H\,(aq) + OH\,-(aq) \quad K_b = K_w/K_a$$

Because acetic acid is a weak acid, its K_a is measurable and $K_b > 0$ (acetate ion is a weak base).

Dissolving sodium acetate in water yields a solution of inert cations (Na^+) and weak base anions ($CH_3CO_2^-$), resulting in a basic solution.

✓ Example 14.7.2: Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with and $[OH^-] = 0.050$ M and $[OH^-] = 2.5 \times 10^{-6} M$ at equilibrium. The reaction is:

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)$$

Solution

The provided equilibrium concentrations and a value for the equilibrium constant will permit calculation of the missing equilibrium concentration. The process in question is the base ionization of acetate ion, for which

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)$$

Substituting the available values into the K_b expression gives

$$K_b = \frac{[CH_3CO_2H]\,[OH^-]}{[CH_3CO_2^-]} = 5.6 \times 10^{-10}$$

$$= \frac{[CH_3CO_2H]\,(2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving the above equation for the acetic acid molarity yields $[CH_3CO_2H] = 1.1 \times 10^{-5}$ M.

? Exercise 14.7.2

What is the pH of a 0.083-*M* solution of NaCN?

Answer

11.11

Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. Likewise, some salts contain a single ion that is amphiprotic, and so the relative strengths of this ion's acid and base character will determine its effect on solution pH. For both types of salts, a comparison of the K_a and K_b values allows prediction of the solution's acid-base status, as illustrated in the following example exercise.

✓ Example 14.7.3: Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. KBr
b. $NaHCO_3$
c. Na_2HPO_4
d. NH_4F

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:

$$\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

Since $K_b \gg K_a$, 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 (see above discussion) 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 1.6×10^{-11}, so the solution is acidic, since $K_a > K_b$.

? Exercise 14.7.3

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. K_2CO_3
b. $CaCl_2$
c. KH_2PO_4
d. $(NH_4)_2CO_3$

Answer

(a) basic; (b) neutral; (c) acidic; (d) basic

The Ionization of Hydrated Metal Ions

Unlike the group 1 and 2 metal ions of the preceding examples (Na^+, Ca^{2+}, etc.), some metal ions function as acids in aqueous solutions. These ions are not just loosely solvated by water molecules when dissolved, instead they are covalently bonded to a fixed number of water molecules to yield a complex ion (see chapter on coordination chemistry). As an example, the dissolution of aluminum nitrate in water is typically represented as

$$Al(NO_3)_3\,(s) \rightleftharpoons Al^{3+}\,(aq) + 3\,NO_3{}^-\,(aq)$$

However, the aluminum(III) ion actually reacts with six water molecules to form a stable complex ion, and so the more explicit representation of the dissolution process is

$$Al(NO_3)_3\,(s) + 6\,H_2O\,(l) \rightleftharpoons Al(H_2O)_6{}^{3+}\,(aq) + 3\,NO_3{}^-\,(aq)$$

As shown in Figure **14.7.1**, the ions involve bonds between a central Al atom and the O atoms of the six water molecules. Consequently, the bonded water molecules' O–H bonds are more polar than in nonbonded water molecules, making the bonded molecules more prone to donation of a hydrogen ion:

$$Al(H_2O)_6{}^{3+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Al(H_2O)_5(OH)^{2+}\,(aq) \qquad K_a = 1.4 \times 10^{-5}$$

The conjugate base produced by this process contains five other bonded water molecules capable of acting as acids, and so the sequential or step-wise transfer of protons is possible as depicted in few equations below:

$$Al(H_2O)_6{}^{3+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Al(H_2O)_5(OH)^{2+}\,(aq)$$
$$Al(H_2O)_5(OH)^{2+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Al(H_2O)_4(OH)_2{}^+\,(aq)$$
$$Al(H_2O)_4(OH)_2{}^+\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Al(H_2O)_3(OH)_3\,(aq)$$

This is an example of a polyprotic acid, the topic of discussion in a later section of this chapter.

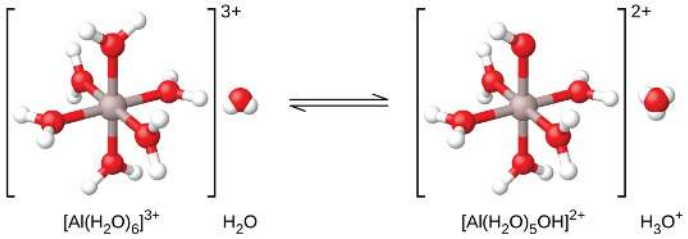


Figure **14.7.1**: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

Aside from the alkali metals (group 1) and some alkaline earth metals (group 2), most other metal ions will undergo acid ionization to some extent when dissolved in water. The acid strength of these complex ions typically increases with increasing charge and decreasing size of the metal ions. The first-step acid ionization equations for a few other acidic metal ions are shown below:

$$Fe(H_2O)_6{}^{3+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Fe(H_2O)_5(OH)^{2+}\,(aq) \qquad pK_a = 2.74$$
$$Cu(H_2O)_6{}^{2+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Cu(H_2O)_5(OH)^{+}\,(aq) \qquad pK_a = \sim 6.3$$
$$Zn(H_2O)_4{}^{2+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Zn(H_2O)_3(OH)^{+}\,(aq) \qquad pK_a = 9.6$$

Example 14.7.4: Hydrolysis of $[Al(H_2O)_6]^{3+}$

Calculate the pH of a 0.10-*M* solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion ($[Al(H_2O)_6]^{3+}$) in solution.

Solution

The equation for the reaction and K_a are:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq) \quad K_a = 1.4 \times 10^{-5}$$

An ICE table with the provided information is

	$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{2+}$		
Initial concentration (*M*)	0.10	~0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$	x	x

Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a = \frac{[H_3O^+]\,[Al(H_2O)_5(OH)^{2+}]}{[Al(H_2O)_6^{3+}]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Assuming $x \ll 0.10$ and solving the simplified equation gives:

$$x = 1.2 \times 10^{-3}\ \text{M}$$

The ICE table defined x as equal to the hydronium ion concentration, and so the pH is calculated to be

$$[H_3O^+] = 0 + x = 1.2 \times 10^{-3}\ \text{M}$$

$$\text{pH} = -\log[H_3O^+] = 2.92$$

Therefore this is an acidic solution.

Exercise 14.7.4

What is $[Al(H_2O)_5(OH)^{2+}]$ in a 0.15-M solution of $Al(NO_3)_3$ that contains enough of the strong acid HNO_3 to bring $[H_3O^+]$ to 0.10 *M*?

Answer

$2.1 \times 10^{-5} M$

This page titled 14.7: Hydrolysis of Salt Solutions is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.4: Hydrolysis of Salt Solutions** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14.8: Polyprotic Acids

Learning Objectives

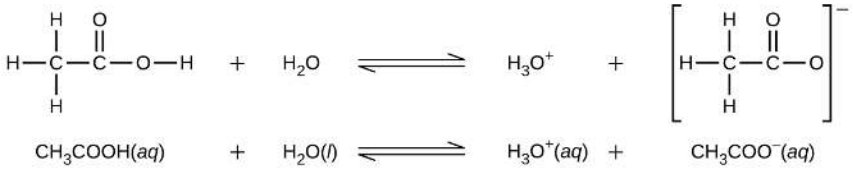
By the end of this section, you will be able to:

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as $\mathbf{HCl}$, $\mathbf{HNO_3}$, and $\mathbf{HCN}$ that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

$$\mathbf{HCl\,(aq) + H_2\,O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$
$$\mathbf{HNO_3\,(aq) + H_2\,O\,(l) \longrightarrow H_3O^+\,(aq) + NO_3^-\,(aq)}$$
$$\mathbf{HCN\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + CN^-\,(aq)}$$

Even though it contains four hydrogen atoms, acetic acid, $\mathbf{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($\mathbf{-COOH}$) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

$$\mathbf{H_2\,SO_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HSO_4^-\,(aq)} \qquad \textbf{(First ionization)}$$

with $K_{a1} > 10^2$.

$$\mathbf{HSO_4^-\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + SO_4^{2-}\,(aq)} \qquad \textbf{(Second ionization)}$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. Carbonic acid, $\mathbf{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

$$\mathbf{H_2\,CO_3\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq)} \qquad \textbf{(First ionization)}$$

with

$$K_{H_2CO_3} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

$$\mathbf{HCO_3^-\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq)} \qquad \textbf{(Second ionization)}$$

with

$$K_{\mathrm{HCO_3^-}} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 4.7 \times 10^{-11}$$

$K_{\mathrm{H_2CO_3}}$ is larger than $K_{\mathrm{HCO_3^-}}$ by a factor of 10^4, so $\mathbf{H_2CO_3}$ is the dominant producer of hydronium ion in the solution. This means that little of the formed by the ionization of $\mathbf{H_2CO_3}$ ionizes to give hydronium ions (and carbonate ions), and the concentrations of $\mathbf{H_3O^+}$ and are practically equal in a pure aqueous solution of $\mathbf{H_2CO_3}$.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This approach is demonstrated in the following example and exercise.

Example 14.8.1: Ionization of a Diprotic Acid

"Carbonated water" contains a palatable amount of dissolved carbon dioxide. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are and in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\,M$?

$$H_2\,CO_3\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq) \quad K_{a2} = 4.7 \times 10^{-11}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than so the stepwise ionization reactions may be treated separately.

The first ionization reaction is

$$H_2\,CO_3\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

Using provided information, an ICE table for this first step is prepared:

	H_2CO_3 +	H_2O $\rightleftharpoons$	H_3O^+ +	HCO_3^-
Initial concentration (*M*)	0.033		~0	0
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.033 - x$		x	x

Substituting the equilibrium concentrations into the equilibrium equation gives

$$K_{H_2CO_3} = \frac{[H3O^+]\,[HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Assuming $x \ll 0.033$ and solving the simplified equation yields

$$x = 1.2 \times 10^{-4}$$

The ICE table defined *x* as equal to the bicarbonate ion molarity and the hydronium ion molarity:

$$[H_2CO_3] = 0.033M$$

$$[H3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}M$$

Using the bicarbonate ion concentration computed above, the second ionization is subjected to a similar equilibrium calculation:

$$HCO_3^-\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq)$$

$$K_{HCO_3^-} = \frac{[H3O^+]\,[CO_3^{2-}]}{[HCO_3^-]} = \frac{(1.2 \times 10^{-4})\,[CO_3^{2-}]}{1.2 \times 10^{-4}}$$

$$[CO_3^{2-}] = \frac{(4.7 \times 10^{-11})\,(1.2 \times 10^{-4})}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11}M$$

To summarize: at equilibrium $[H_2CO_3] = 0.033M$; $[H_3O^+] = 1.2 \times 10^{-4}$; $[HCO_3^-] = 1.2 \times 10^{-4}\,M$; $[CO_{32}^-] = 4.7 \times 10^{-11}\,M$.

Exercise 14.8.1

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate, H_3O^+, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer

$[H_2S] = 0.1\,M$

$[H_3O^+] = [HS^-] = 0.000094\,M$

$[S^{2-}] = 1 \times 10^{-19}\,M$

A **triprotic acid** is an acid that has three ionizable H atoms. Phosphoric acid is one example:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \quad \text{(First ionization)}$$
$$K_{a1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \quad \text{(Second ionization)}$$
$$K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \quad \text{(Third ionization)}$$
$$K_{a3} = 4.2 \times 10^{-13}$$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former, reflected in decreasing values for the stepwise acid ionization constants. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6.

This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, large differences exist in the small changes in concentration accompanying the ionization reactions. This allows the use of math-simplifying assumptions and processes, as demonstrated in the examples above.

Polyprotic bases are capable of accepting more than one hydrogen ion. The carbonate ion is an example of a **diprotic base**, because it can accept two protons, as shown below. Similar to the case for polyprotic acids, note the ionization constants decrease with ionization step. Likewise, equilibrium calculations involving polyprotic bases follow the same approaches as those for polyprotic acids.

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \quad K_{b1} = 2.1 \times 10^{-4}$$

$$H_2O(l) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \quad K_{b2} = 2.3 \times 10^{-8}$$

This page titled 14.8: Polyprotic Acids is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.5: Polyprotic Acids** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14.9: Buffers

Learning Objectives

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

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure **14.9.1**). A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq)$ + $NH_4Cl(aq)$).



Figure **14.9.1**: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, strong base added to this solution will neutralize hydronium ion, causing the acetic acid ionization equilibrium to shift to the right and generate additional amounts of the weak conjugate base (acetate ion):

$$\mathrm{CH_3\,CO_2\,H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3\,CO_2^-\,(aq)}$$

Likewise, strong acid added to this buffer solution will shift the above ionization equilibrium left, producing additional amounts of the weak conjugate acid (acetic acid). Figure **14.9.2** provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

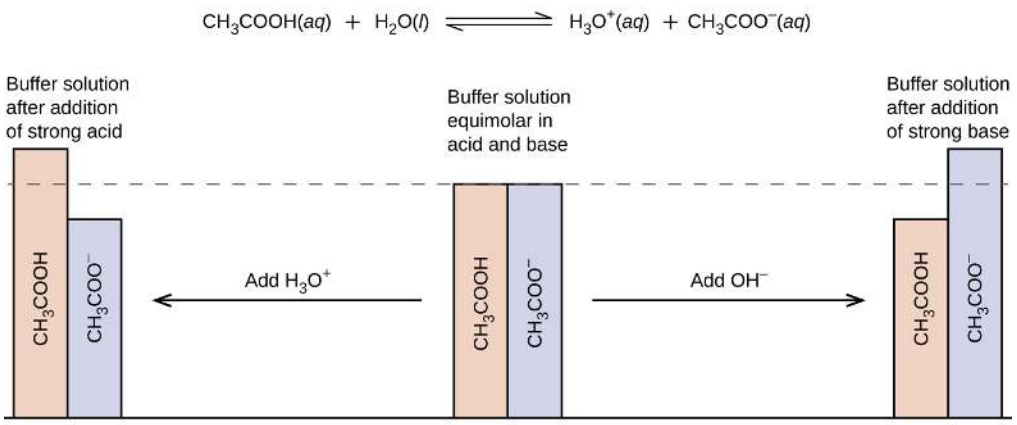


Figure 14.9.2: Buffering action in a mixture of acetic acid and acetate salt.

Example 14.20: pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 NaOH is added to 100 mL of this buffer.
c. For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

Solution

(a) Following the ICE approach to this equilibrium calculation yields the following:

	CH_3CO_2H +	H_2O ⇌	H_3O^+ +	$CH_3CO_2^-$
Initial concentration (*M*)	0.10		~0	0.10
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$		x	$0.10 + x$

Substituting the equilibrium concentration terms into the K_a expression, assuming $x \ll 0.10$, and solving the simplified equation for x yields

$$x = 1.8 \times 10^{-5}\ \text{M}$$

$$[\text{H}_3\text{O}^+] = 0 + x = 1.8 \times 10^{-5}\ \text{M}$$

$$\begin{aligned} pH &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.8 \times 10^{-5}) \\ &= 4.74 \end{aligned}$$

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer.

Adding strong base will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

$$0.0010\ \cancel{\text{L}} \times \left(\frac{0.10\ \text{mol NaOH}}{1\ \cancel{\text{L}}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

The initial molar amount of acetic acid is

$$0.100 \cancel{L} \times \left(\frac{0.100 \text{ mol } CH_3CO_2H}{1 \cancel{L}} \right) = 1.00 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The amount of acetic acid remaining after some is neutralized by the added base is

$$\left(1.0 \times 10^{-2}\right) - \left(0.01 \times 10^{-2}\right) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

$$\left(1.0 \times 10^{-2}\right) + \left(0.01 \times 10^{-2}\right) = 1.01 \times 10^{-2} \text{ mol } NaCH_3CO_2$$

Compute molar concentrations for the two buffer components:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \text{ M}$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \text{ M}$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

The amount of hydronium ion initially present in the solution is

$$[H_3O^+] = 10^{-4.74} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{mol } H_3O^+ = (0.100 \text{ L})\left(1.8 \times 10^{-5} \text{ M}\right) = 1.8 \times 10^{-6} \text{ mol } H_3O^+$$

The amount of hydroxide ion added to the solution is

$$molOH^- = (0.0010L)(0.10M) = 1.0 \times 10^{-4} molOH^-$$

The added hydroxide will neutralize hydronium ion via the reaction

$$H_3O^+(aq) + OH^-(aq) \ \mhchemleftrightharpoons 2\,H_2O(l)$$

The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining is

$$1.0 \times 10^{-4} mol - 1.8 \times 10^{-6} mol = 9.8 \times 10^{-5} molOH^-$$

corresponding to a hydroxide molarity of

$$\frac{9.8 \times 10^{-5} \text{ mol } OH^-}{0.101 \text{ L}} = 9.7 \times 10^{-4} M$$

The pH of the solution is then calculated to be

$$pH = 14.00 - pOH = 14.00 - -\log\left(9.7 \times 10^{-4}\right) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 to 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

? Exercise 14.9.1

Show that adding 1.0 mL of $0.10 \text{ M } HCl$ changes the pH of 100 mL of a $1.8 \times 10^{-5} \text{ M } HCl$ solution from 4.74 to 3.00.

Answer

Initial pH of $1.8 \times 10^{-5} \text{ M } HCl$;

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$$

Moles of H_3O^+ in 100 mL 1.8×10^{-5} M HCl;

$$(1.8 \times 10^{-5} \text{ moles/L}) \times (0.100 \text{ L} = 1.8 \times 10^{-6} \text{ mol}$$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl:

$$(0.10 \text{ moles/L}) \times (0.0010 \text{ L}) = 1.0 \times 10^{-4} \text{ mol}$$

Final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$pH = -\log\left[\text{H}_3\text{O}^+\right] = -\log\left(\frac{\text{total moles } \text{H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4} mol + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}\right) = 3.00$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure **14.9.3**). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.



Figure **14.9.3**: 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 affect 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 unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are 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 more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure **14.9.4** shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

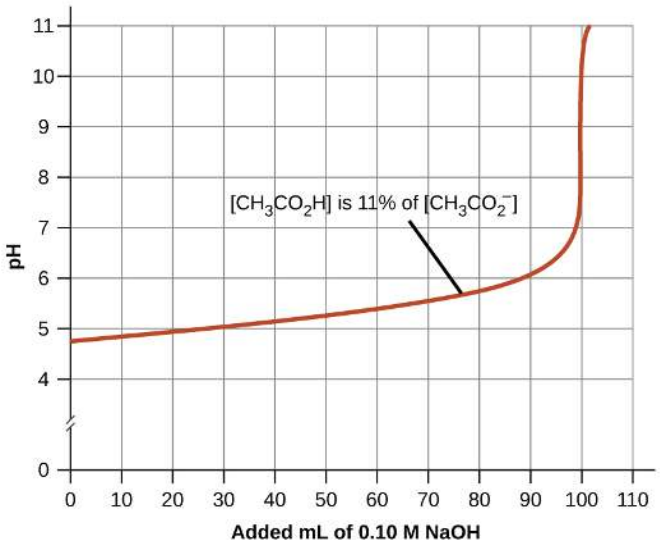


Figure **14.9.4**: Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H]$ = 0.10 *M* and Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, $\mathbf{H_2CO_3}$, and the bicarbonate ion, $\mathbf{HCO_3^-}$. When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

$$\mathbf{H_3O^+\,(aq) + HCO_3^-\,(aq) \longrightarrow H_2\,CO_3\,(aq) + H_2O\,(l)}$$

An added hydroxide ion is removed by the reaction:

$$\mathbf{OH^-\,(aq) + H_2CO_3\,(aq) \longrightarrow HCO_3^-\,(aq) + H_2O\,(l)}$$

The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair (H_3O^+ is converted to H_2CO_3 and OH^- is converted to HCO_3^-). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[\mathbf{H_3O^+}]\,[\mathbf{A^-}]}{[\mathbf{HA}]}$$

Rearranging to solve for $[H_3O^+]$ yields:

$$[\mathbf{H_3O^+}] = K_a \times \frac{[\mathbf{HA}]}{[\mathbf{A^-}]}$$

Taking the negative logarithm of both sides of this equation gives

$$-\log\,[\mathbf{H_3O^+}] = -\log K_a - \log \frac{[\mathbf{HA}]}{[\mathbf{A^-}]}$$

which can be written as

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

where pK_a is the negative of the logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch equation, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

Portrait of a Chemist: Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

How Sciences Interconnect: Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2\,(g) + 2\,H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)}$$

The concentration of carbonic acid, $\mathrm{H_2CO_3}$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$pH = pK_a + \log\frac{[\text{ base }]}{[\text{ acid }]} = 6.4 + \log\frac{0.024}{0.0012} = 7.7$$

The fact that the $\mathrm{H_2CO_3}$ concentration is significantly lower than that of the $\mathrm{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Link to Learning

View information on the buffer system encountered in natural waters.

This page titled 14.9: Buffers is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.6: Buffers** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14.10: Acid-Base Titrations

Learning Objectives

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

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the underlying chemical equilibria that make acid-base titrimetry a useful analytical technique.

Titration Curves

A titration curve is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point. The following example exercise demonstrates the computation of pH for a titration solution after additions of several specified titrant volumes. The first example involves a strong acid titration that requires only stoichiometric calculations to derive the solution pH. The second example addresses a weak acid titration requiring equilibrium calculations.

Example 14.10.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH (the titration curve is shown in Figure 14.10.1). Calculate the pH at these volumes of added base solution:

a. 0.00 mL
b. 12.50 mL
c. 25.00 mL
d. 37.50 mL

Solution

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 *M*. The pH of the solution is then

$$\mathrm{pH} = -\log(0.100) = 1.000$$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining is computed by subtracting the consumed amount from the initial amount and then dividing by the solution volume:

$$[\mathrm{H_3O^+}] = \frac{n(\mathrm{H^+})}{V} = \frac{0.002500\ \mathrm{mol} \times \left(\frac{1000\ mL}{1\ L}\right) - 0.100\ M \times 12.50\ mL}{25.00\ mL + 12.50\ mL} = 0.0333\ M$$

(c) Titrant volume = 25.00 mL. This titrant addition involves a stoichiometric amount of base (the *equivalence point*), and so only products of the neutralization reaction are in solution (water and NaCl). Neither the cation nor the anion of this salt undergo acid-base ionization; the only process generating hydronium ions is the autoprotolysis of water. The solution is neutral, having a pH = 7.00.

(d) Titrant volume = 37.50 mL. This involves the addition of titrant in excess of the equivalence point. The solution pH is then calculated using the concentration of hydroxide ion:

$$n(OH^-)_0 > n(H^+)_0$$

$$[OH^-] = \frac{n(OH^-)}{V} = \frac{0.100\ M \times 37.50\ mL - 0.002500\ mol \times \left(\frac{1000\ mL}{1\ L}\right)}{25.00\ mL + 37.50\ mL} = 0.0200\ M$$

$$pH = 14 - pOH = 14 + \log([OH^-]) = 14 + \log(0.0200) = 12.30$$

Exercise 14.10.1

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $HNO_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

Answer

0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

Example 14.10.2: Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O$$

Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

a. 0.00 mL
b. 25.00 mL
c. 12.50 mL
d. 37.50 mL

Solution

(a) The initial pH is computed for the acetic acid solution in the usual ICE approach:

$$K_a = \frac{[H3O^+]\,[CH_3CO_2^-]}{[CH_3CO_2H]} \approx \frac{[H3O^+]^2}{[CH_3CO_2H]_0}$$

and

$$[H3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log\left(1.3 \times 10^{-3}\right) = 2.87$$

(b) The acid and titrant are both monoprotic and the sample and titrant solutions are equally concentrated; thus, this volume of titrant represents the equivalence point. Unlike the strong-acid example above, however, the reaction mixture in this case contains a weak conjugate base (acetate ion). The solution pH is computed considering the base ionization of acetate, which is present at a concentration of

$$\frac{0.00250\ mol}{0.0500\ L} = 0.0500\ M\ CH_3CO_2^-$$

Base ionization of acetate is represented by the equation

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

$$K_b = \frac{[H^+]\,[OH^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Assuming $x \ll 0.0500$, the pH may be calculated via the usual ICE approach:

$$K_b = \frac{x^2}{0.0500M}$$

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$\text{pOH} = -\log\left(5.3 \times 10^{-6}\right) = 5.28$$
$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7, as expected when titrating a weak acid with a strong base.

(c) Titrant volume = 12.50 mL. This volume represents one-half of the stoichiometric amount of titrant, and so one-half of the acetic acid has been neutralized to yield an equivalent amount of acetate ion. The concentrations of these conjugate acid-base partners, therefore, are equal. A convenient approach to computing the pH is use of the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{ Base }]}{[\text{ Acid }]} = -\log\left(K_a\right) + \log\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = -\log\left(1.8 \times 10^{-5}\right) + \log(1)$$

$$pH = -\log\left(1.8 \times 10^{-5}\right) = 4.74$$

(pH = pK_a at the half-equivalence point in a titration of a weak acid)

(d) Titrant volume = 37.50 mL. This volume represents a stoichiometric excess of titrant, and a reaction solution containing both the titration product, acetate ion, and the excess strong titrant. In such solutions, the solution pH is determined primarily by the amount of excess strong base:

$$[\text{OH}^-] = \frac{(0.003750mol - 0.00250mol)}{0.06250L} = 2.00 \times 10^{-2}M$$

$$\text{pOH} = -\log\left(2.00 \times 10^{-2}\right) = 1.70$$
$$\text{pH} = 14.00 - 1.70 = 12.30$$

? Exercise 14.10.1

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

Answer

0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

Performing additional calculations similar to those in the preceding example permits a more full assessment of titration curves. A summary of pH/volume data pairs for the strong and weak acid titrations is provided in Table **14.10.1** and plotted as titration curves in Figure **14.10.1**. A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

- initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated; because the two acid samples are equally concentrated, the weak acid will exhibit a greater initial pH
- pre-equivalence point (0 mL < *V* < 25 mL): solution pH increases gradually and the acid is consumed by reaction with added titrant; composition includes unreacted acid and the reaction product, its conjugate base
- equivalence point (*V* = 25 mL): a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral (for the strong acid sample) or basic (for the weak acid sample), with pH determined by ionization of the conjugate base of the acid
- postequivalence point (*V* > 25 mL): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

Table **14.10.1**: pH Values in the Titrations of a Strong Acid and of a Weak Acid

Volume of 0.100 *M* NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 *M* HCl[1]	pH Values 0.100 *M* CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

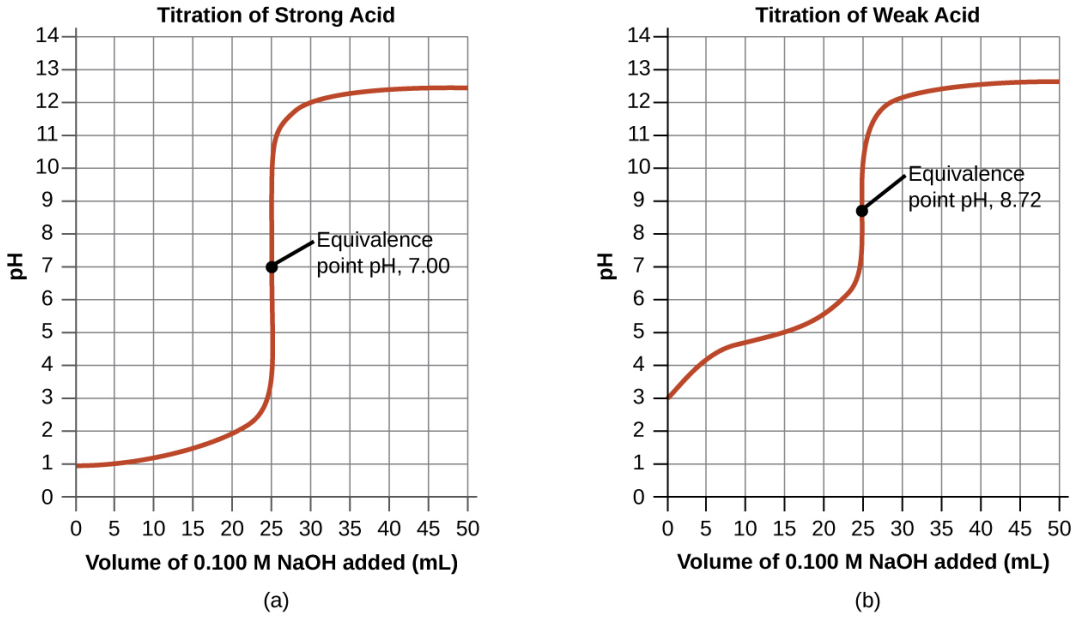


Figure **14.10.1**: (a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 8.72 pH.

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} M (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} M (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underset{\text{red}}{\mathrm{HIn(aq)}} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \underset{\text{yellow}}{In^-(aq)}$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{In^-}]}{[\mathrm{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, $\mathrm{In^-}$, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

The perceived color of an indicator solution is determined by the ratio of the concentrations of the two species $\mathrm{In^-}$ and HIn. If most of the indicator (typically about 60−90% or more) is present as $\mathrm{In^-}$, the perceived color of the solution is yellow. If most is present as HIn, then the solution color appears red. The Henderson-Hasselbalch equation is useful for understanding the relationship between the pH of an indicator solution and its composition (thus, perceived color):

$$pH = pKa + \log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right)$$

In solutions where pH > pK_a, the logarithmic term must be positive, indicating an excess of the conjugate base form of the indicator (yellow solution). When pH < pK_a, the log term must be negative, indicating an excess of the conjugate acid (red solution). When the solution pH is close to the indicator pKa, appreciable amounts of both conjugate partners are present, and the solution color is that of an additive combination of each (yellow and red, yielding orange). The **color change interval** (or *pH interval*) for an acid-

base indicator is defined as the range of pH values over which a change in color is observed, and for most indicators this range is approximately pK_a ± 1.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure **14.10.2** presents several indicators, their colors, and their color-change intervals.

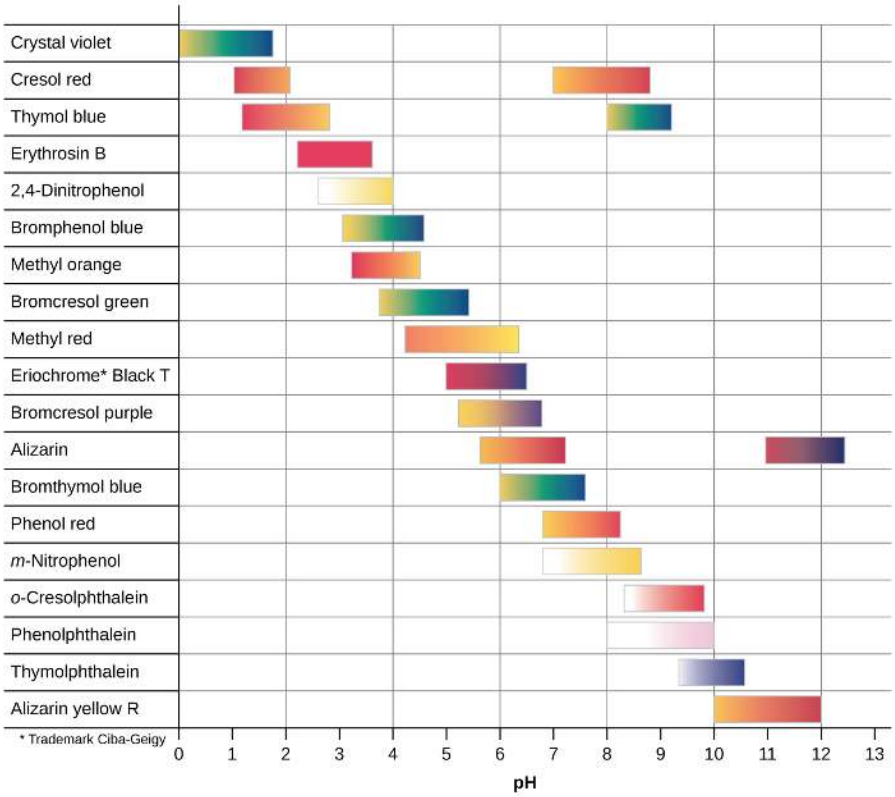


Figure **14.10.2**: This chart illustrates the color change intervals for several acid-base indicators.

The titration curves shown in Figure **14.10.3** illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

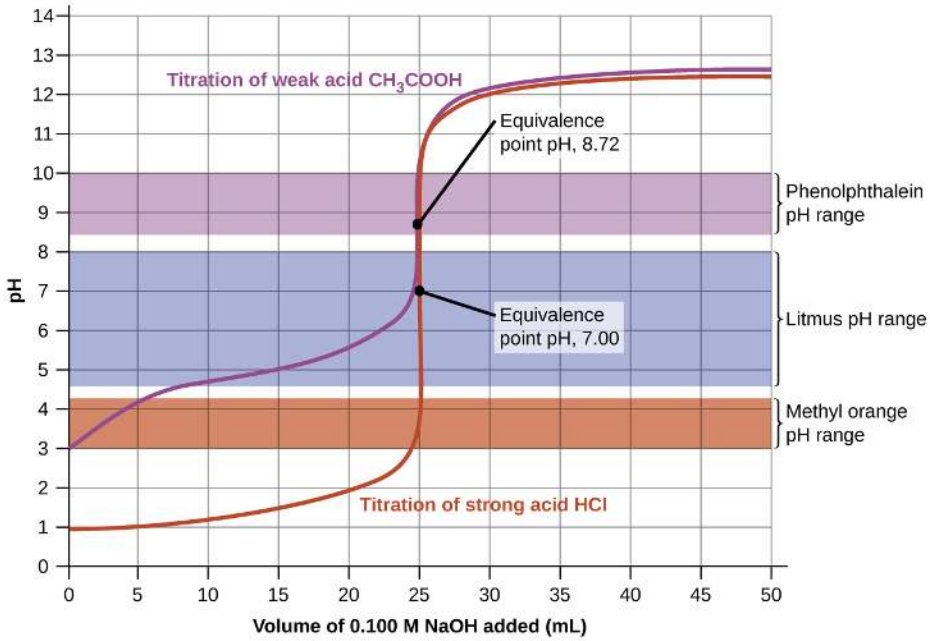


Figure **14.10.3**: Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The weak acid titration curve in Figure **14.10.3** shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.

Footnotes

- 1Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
- 2Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

This page titled 14.10: Acid-Base Titrations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **14.7: Acid-Base Titrations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

14.11: Key Terms

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 an acid ionization reaction

acid-base indicator | weak acid or base whose conjugate partner imparts a different solution color; used in visual assessments of solution pH

acidic | a solution in which $[H_3O^+] > [OH^-]$

amphiprotic | species that may either donate or accept a proton in a Bronsted-Lowry acid-base reaction

amphoteric | species that can act as either an acid or a base

autoionization | reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization | reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

base ionization constant (K_b) | equilibrium constant for a base ionization reaction

basic | a solution in which $[H_3O^+] < [OH^-]$

Brønsted-Lowry acid | proton donor

Brønsted-Lowry base | proton acceptor

buffer | mixture of appreciable amounts of a weak acid-base pair 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)

color-change interval | range in pH over which the color change of an indicator is observed

conjugate acid | substance formed when a base gains a proton

conjugate base | substance formed when an acid loses a proton

diprotic acid | acid containing two ionizable hydrogen atoms per molecule

diprotic base | base capable of accepting two protons

Henderson-Hasselbalch equation | logarithmic version of the acid ionization constant expression, conveniently formatted for calculating the pH of buffer solutions

ion-product constant for water (K_w) | equilibrium constant for the autoionization of water

leveling effect | observation that acid-base strength of solutes in a given solvent is limited to that of the solvent's characteristic acid and base species (in water, hydronium and hydroxide ions, respectively)

monoprotic acid | acid containing one ionizable hydrogen atom per molecule

neutral | describes a solution in which $[H_3O^+] = [OH^-]$

oxyacid | ternary compound with acidic properties, molecules of which contain a central nonmetallic atom bonded to one or more O atoms, at least one of which is bonded to an ionizable H atom

percent ionization | ratio of the concentration of ionized acid to initial acid concentration expressed as a percentage

pH | logarithmic measure of the concentration of hydronium ions in a solution

pOH | logarithmic measure of the concentration of hydroxide ions in a solution

stepwise ionization | process in which a polyprotic acid is ionized by losing protons sequentially

titration curve | plot of some sample property (such as pH) versus volume of added titrant

triprotic acid | acid that contains three ionizable hydrogen atoms per molecule

14.11: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **14.8: Key Terms** is licensed CC BY 4.0.

14.12: Key Equations

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)

$pOH = -\log[OH^-]$
$[H_3O^+] = \times 10^{-pH}$
$[OH^-] = \times 10^{-pOH}$
$pH + pOH = pK_w = 14.00$ at 25 °C

$K_a K_b = 1.0 \times 10^{-14} = K_w$

$pK_a = -\log K_a$
$pK_b = -\log K_b$

14.12: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **14.9: Key Equations** is licensed CC BY 4.0.

CHAPTER OVERVIEW

15: Equilibria of Other Reaction Classes

We previously learned about aqueous solutions and their importance, as well as about solubility rules. While this gives us a picture of solubility, that picture is not complete if we look at the rules alone. Solubility equilibrium, which we will explore in this chapter, is a more complex topic that allows us to determine the extent to which a slightly soluble ionic solid will dissolve, and the conditions under which precipitation.

15.1: Introduction
15.2: Precipitation and Dissolution
15.3: Lewis Acids and Bases
15.4: Coupled Equilibria
15.5: Key Terms
15.6: Key Equations
15.7: Summary
15.8: Exercises

This page titled 15: Equilibria of Other Reaction Classes is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

15.1: Introduction

The mineral fluorite, CaF_2 Figure **15.1.1**: , is commonly used as a semiprecious stone in many types of jewelry because of its striking appearance. Deposits of fluorite are formed through a process called hydrothermal precipitation in which calcium and fluoride ions dissolved in groundwater combine to produce insoluble CaF_2 in response to some change in solution conditions. For example, a decrease in temperature may trigger fluorite precipitation if its solubility is exceeded at the lower temperature. Because fluoride ion is a weak base, its solubility is also affected by solution pH, and so geologic or other processes that change groundwater pH will also affect the precipitation of fluorite. This chapter extends the equilibrium discussion of other chapters by addressing some additional reaction classes (including precipitation) and systems involving coupled equilibrium reactions.

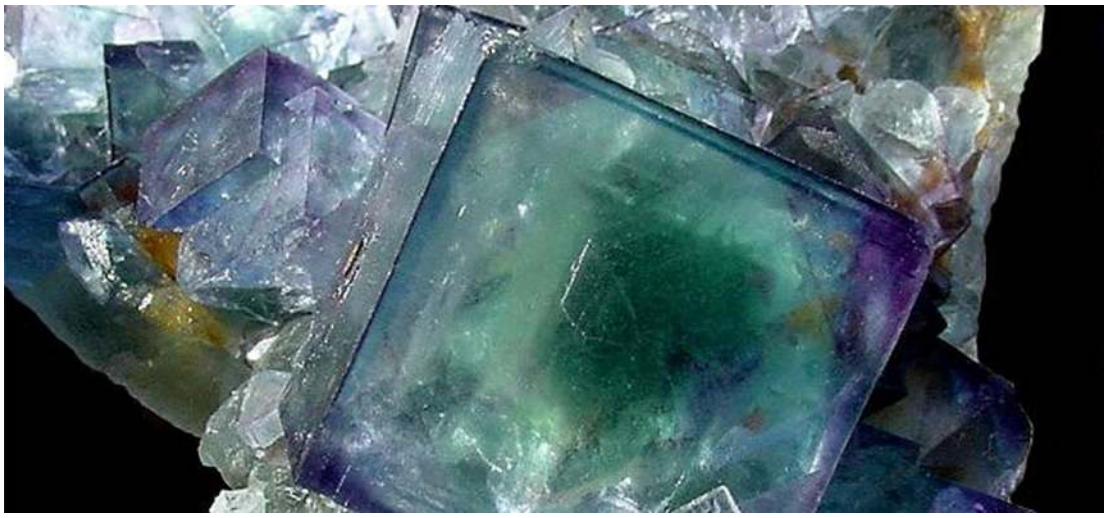


Figure **15.1.1**: The mineral fluorite (CaF_2) is formed when dissolved calcium and fluoride ions precipitate from groundwater within the Earth's crust. Note that pure fluorite is colorless, and that the color in this sample is due to the presence of other metal ions in the crystal.

15.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **15.0: Introduction** is licensed CC BY 4.0.

15.2: Precipitation and Dissolution

Learning Objectives

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

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

Solubility equilibria are established when the dissolution and precipitation of a solute species occur at equal rates. These equilibria underlie many natural and technological processes, ranging from tooth decay to water purification. An understanding of the factors affecting compound solubility is, therefore, essential to the effective management of these processes. This section applies previously introduced equilibrium concepts and tools to systems involving dissolution and precipitation.

The Solubility Product

Recall from the chapter on solutions that the solubility of a substance can vary from essentially zero (*insoluble* or *sparingly soluble*) to infinity (*miscible*). A solute with finite solubility can yield a *saturated* solution when it is added to a solvent in an amount exceeding its solubility, resulting in a heterogeneous mixture of the saturated solution and the excess, undissolved solute. For example, a saturated solution of silver chloride is one in which the equilibrium shown below has been established.

$$\mathrm{AgCl(s)} \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Ag^+(aq) + Cl^-(aq)}$$

In this solution, an excess of solid AgCl dissolves and dissociates to produce aqueous $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$ ions at the same rate that these aqueous ions combine and precipitate to form solid AgCl (Figure 15.2.1). Because silver chloride is a sparingly soluble salt, the equilibrium concentration of its dissolved ions in the solution is relatively low.

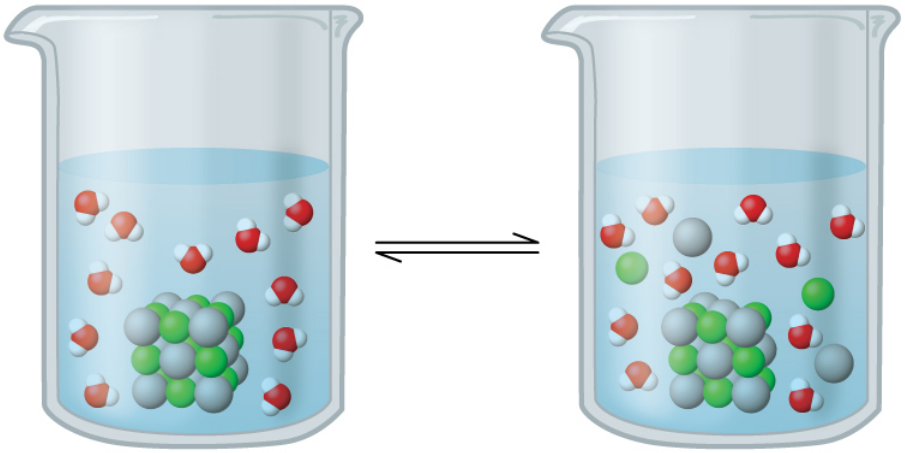


Figure 15.2.1: Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

The equilibrium constant for solubility equilibria such as this one is called the **solubility product constant, K_{sp}**, in this case

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq) + Cl^-(aq)} \qquad K_{sp} = [\mathrm{Ag^+(aq)}]\,[\mathrm{Cl^-(aq)}]$$

Recall that only gases and solutes are represented in equilibrium constant expressions, so the K_{sp} does not include a term for the undissolved AgCl. A listing of solubility product constants for several sparingly soluble compounds is provided in Appendix J.

Example 15.2.1: 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. $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids
c. $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia
d. $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium
e. $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

Solution

a. $\mathrm{AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)}$

$$K_{sp} = [Ag^+]\,[I^-]$$

b. $\mathrm{CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)}$

$$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}]$$

c. $\mathrm{Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)}$

$$K_{sp} = [Mg^{2+}]\,[OH^-]^2$$

d. $\mathrm{Mg(NH_4)PO_4(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq)}$

$$K_{sp} = [Mg^{2+}]\,[NH_4^+]\,[PO_4^{3-}]$$

e. $\mathrm{Ca_5(PO_4)\,3\,OH(s) \rightleftharpoons 5\,Ca^{2+}(aq) + 3\,PO_4^{3-}(aq) + OH^-(aq)}$

$$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$$

Exercise 15.2.1

Write the dissolution equation and the solubility product for each of the following slightly soluble compounds:

a. $BaSO_4$
b. Ag_2SO_4
c. $Al(OH)_3$
d. Pb(OH)Cl

Answer

a. $\mathrm{BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)}$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

b. $\mathrm{Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4^{2-}(aq)}$

$$K_{sp} = [Ag^+]^2\,[SO_4^{2-}]$$

c. $\mathrm{Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)}$

$$K_{sp} = [Al^{3+}]\,[OH^-]^3$$

d. $\mathrm{Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^-(aq) + Cl^-(aq)}$

$$K_{sp} = [Pb^{2+}]\,[OH^-]\,[Cl^-]$$

K_{sp} and Solubility

The K_{sp} of a slightly soluble ionic compound may be simply related to its measured solubility provided the dissolution process involves only dissociation and solvation, for example:

$$\mathrm{M_pX_q\,(s) \rightleftharpoons p\ M^{m+}\,(aq) + q\ X^{n-}\,(aq)}$$

For cases such as these, one may derive K_{sp} values from provided solubilities, or vice-versa. Calculations of this sort are most conveniently performed using a compound's molar solubility, measured as moles of dissolved solute per liter of saturated solution.

Example 15.2.2: Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, $\mathrm{CaF_2}$, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)}$$

The concentration of $\mathrm{Ca^{2+}}$ in a saturated solution of $\mathrm{CaF_2}$ is 2.15×10^{-4} M. What is the solubility product 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:

$$[F^-] = \left(2\ \mathrm{mol\ F^-}/1\ \mathrm{mol\ Ca^{2+}}\right) = (2)\left(2.15 \times 10^{-4} M\right) = 4.30 \times 10^{-4} M$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = \left[\mathrm{Ca^{2+}}\right]\left[\mathrm{F^-}\right]^2 = \left(2.15 \times 10^{-4}\right)\left(4.30 \times 10^{-4}\right)^2 = 3.98 \times 10^{-11}$$

Exercise 15.2.2

In a saturated solution of $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31×10^{-4} M. What is the solubility product for $Mg(OH)_2$?

$$\mathrm{Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

Answer

8.99×10^{-12}

Example 15.2.3: 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

$$\mathrm{CuBr\,(s) \rightleftharpoons Cu^+(aq)^+\ Br^-\,(aq)}$$

with

$$K_{sp} = \left[\mathrm{Cu^+}\right]\left[\mathrm{Br^-}\right]$$

Following the ICE approach to this calculation yields the table

	CuBr (s) $\rightleftharpoons$	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

$$\begin{aligned} K_{sp} &= [\mathrm{Cu^+}]\,[\mathrm{Br^-}] \\ 6.3 \times 10^{-9} &= (x)(x) = x^2 \\ x &= \sqrt{6.3 \times 10^{-9}} \\ &= 7.9 \times 10^{-5}\ \mathrm{M} \end{aligned}$$

Since the dissolution stoichiometry shows one mole of copper(I) ion and one mole of bromide ion are produced for each moles of **Br** dissolved, the molar solubility of **CuBr** is 7.9×10^{-5} **M**.

? Exercise 15.2.3

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer

1.2×10^{-8} **M**

✓ Example 15.2.4: Determination of Molar Solubility from K_{sp}

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$\mathrm{Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

with

$$K_{sp} = [\mathrm{Ca^{2+}}]\,[\mathrm{OH^-}]^2$$

The ICE table for this system is

	$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq)$	+	$2OH^-\,(aq)$
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

$$\begin{aligned} K_{sp} &= [\mathrm{Ca^{2+}}]\,[\mathrm{OH^-}]^2 \\ 1.3 \times 10^{-6} &= (x)(2x)^2 = (x)\left(4x^2\right) = 4x^3 \\ x &= \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} \\ &= 6.9 \times 10^{-3}\ \mathrm{M} \end{aligned}$$

As defined in the ICE table, x is the molarity of calcium ion in the saturated solution. The dissolution stoichiometry shows a 1:1 relation between moles of calcium ion in solution and moles of compound dissolved, and so, the molar solubility of $Ca(OH)_2$ is 6.9×10^{-3} **M**.

Exercise 15.2.4

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer

1.5×10^{-3} M

Example 15.2.5: Determination of K_{sp} from Gram Solubility

Many of the pigments used by artists in oil-based paints (Figure 15.2.2) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product for $PbCrO_4$.



Figure 15.2.2: 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:

$$[PbCrO_4] = \frac{4.6 \times 10^{-6}\ \text{g PbCrO4}}{1\ \text{L}} \times \frac{1\ \text{mol PbCrO}_4}{323.2\ \text{g PbCrO}_4}$$

$$= \frac{1.4 \times 10^{-8}\ \text{mol PbCrO}_4}{1\ \text{L}}$$

$$= 1.4 \times 10^{-8}\ \text{M}$$

The dissolution equation for this compound is

$$PbCrO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + {CrO_4}^{2-}\,(aq)$$

The dissolution stoichiometry shows a 1:1 relation between the molar amounts of compound and its two ions, and so both $[Pb^{2+}]$ and $[{CrO_4}^{2-}]$ are equal to the molar solubility of $PbCrO_4$:

$$[Pb^{2+}] = [{CrO_4}^{2-}] = 1.4 \times 10^{-8}\ \text{M}$$

Therefore

$$K_{sp} = [Pb^{2+}][{CrO_4}^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$$

Exercise 15.2.5

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.12 grams per liter at 20 °C. What is its solubility product?

Answer

1.69×10^{-4}

Example 15.2.6: Calculating the Solubility of Hg_2Cl_2

Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I), and chloride ions, Cl^-. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel has a very low solubility, as suggested by its very small K_{sp}:

$$\mathrm{Hg_2Cl_2\,(s) \rightleftharpoons Hg_2^{2+}\,(aq) + 2\,Cl^-\,(aq)} \quad K_{sp} = 1.1 \times 10^{-18}$$

Calculate the molar solubility of $\mathrm{Hg_2Cl_2}$.

Solution

The dissolution stoichiometry shows a 1:1 relation between the amount of compound dissolved and the amount of mercury(I) ions, and so the molar solubility of Hg_2Cl_2 is equal to the concentration of ions

Following the ICE approach results in

	$\mathrm{Hg_2Cl_2\,(s) \rightleftharpoons Hg_2^{2+}\,(aq)}$	+	$\mathrm{2Cl^-\,(aq)}$
Initial concentration (M)		0	0
Change (M)		$+x$	$+2x$
Equilibrium concentration (M)		x	$2x$

Substituting the equilibrium concentration terms into the solubility product expression and solving for x gives

$$\begin{aligned} K_{sp} &= [\mathrm{Hg_2^{2+}}]\,[\mathrm{Cl^-}]^2 \\ 1.1 \times 10^{-18} &= (x)(2x)^2 \\ 4x^3 &= 1.1 \times 10^{-18} \\ x &= \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} \\ &= 6.5 \times 10^{-7}\ \mathrm{M} \end{aligned}$$

Therefore

$$\begin{aligned} [\mathrm{Hg_2^{2+}}] &= 6.5 \times 10^{-7}\ \mathrm{M} \\ &= 6.5 \times 10^{-7}\ \mathrm{M} \\ [\mathrm{Cl^-}] &= 2x = 2\left(6.5 \times 10^{-7}\ \mathrm{M}\right) \\ &= 1.3 \times 10^{-6} M \end{aligned}$$

The dissolution stoichiometry shows the molar solubility of $\mathrm{Hg_2Cl_2}$ is equal to $[\mathrm{Hg_2^{2+}}]$ or 6.5×10^{-7} M.

Exercise 15.2.6

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

Answer

1.2×10^{-3} M

How Sciences Interconnect: Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 2.3×10^{-8}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 15.2.3).



Figure 15.2.3: 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)

Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Visit this website for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3{}^{2-}\,(aq)$$

with

$$K_{sp} = \left[Ca^{2+}\right]\left[CO_3{}^{2-}\right] = 8.7 \times 10^{-9}$$

It is important to realize that this equilibrium is established in any aqueous solution containing Ca^{2+} and $CO_3{}^{2-}$ ions, not just in a solution formed by saturating water with calcium carbonate. Consider, for example, mixing aqueous solutions of the soluble compounds sodium carbonate and calcium nitrate. If the concentrations of calcium and carbonate ions in the mixture do not yield a reaction quotient, Q_{sp}, that exceeds the solubility product, K_{sp}, then no precipitation will occur. If the ion concentrations yield a reaction quotient greater than the solubility product, then precipitation will occur, lowering those concentrations until equilibrium is established ($Q_{sp} = K_{sp}$). The comparison of Q_{sp} to K_{sp} to predict precipitation is an example of the general approach to predicting the direction of a reaction first introduced in the chapter on equilibrium. For the specific case of solubility equilibria:

- $Q_{sp} < K_{sp}$: the reaction proceeds in the forward direction (solution is not saturated; no precipitation observed)
- $Q_{sp} > K_{sp}$: the reaction proceeds in the reverse direction (solution is supersaturated; precipitation will occur)

This predictive strategy and related calculations are demonstrated in the next few example exercises.

Example 15.2.7: Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$\mathrm{Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,OH^-\,(aq)} \quad K_{sp} = 8.9 \times 10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\mathrm{Mg^{2+}}]\,[\mathrm{OH^-}]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because *Q* is greater than K_{sp} (\(Q = 5.4 \times 10^{–8}\) is larger than $K_{sp} = 8.9 \times 10^{-12}$), the reverse reaction will proceed, precipitating magnesium hydroxide until the dissolved ion concentrations have been sufficiently lowered, so that $Q_{sp} = K_{sp}$.

Exercise 15.2.7

Predict whether $\mathrm{CaHPO_4}$ will precipitate from a solution with $[Ca^{2+}]$ = 0.0001 *M* and = 0.001 *M*.

Answer

No precipitation of $\mathrm{CaHPO_4}$; $Q = 1 \times 10^{-7}$, which is less than K_{sp} (7×10^{-7})

Example 15.2.8: Precipitation of AgCl

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}-M solution of AgNO3 and a 2.0×10^{-4}-M solution of NaCl are mixed?

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$\mathrm{AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)}$$

The solubility product is 1.6×10^{-10} (see appendix J).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. Because the volume doubles when equal volumes of $AgNO_3$ and NaCl solutions are mixed, each concentration is reduced to half its initial value

$$\frac{1}{2}\,(2.0 \times 10^{-4})\,M = 1.0 \times 10^{-4}\ \mathrm{M}$$

The reaction quotient, *Q*, is greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [\mathrm{Ag^+}]\,[\mathrm{Cl^-}] = (1.0 \times 10^{-4})\,(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

AgCl will precipitate from the mixture until the dissolution equilibrium is established, with *Q* equal to K_{sp}.

Exercise 15.2.8

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of ClO_4^-? (Hint: Use the dilution equation to calculate the concentrations of potassium and perchlorate ions in the mixture.)

Answer

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$

Example 15.2.9: Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 15.2.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (calcium oxalate monohydrate). The concentration of Ca^{2+} in a sample of blood serum is $2.2 \times 10^{-3} M$. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4 \cdot H_2O$ begins to precipitate?



Figure 15.2.4: Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

For this reaction:

$$K_{sp} = [Ca^{2+}]\,[C_2O_4^{2-}] = 1.96 \times 10^{-9}$$

(see Appendix J)

Substitute the provided calcium ion concentration into the solubility product expression and solve for oxalate concentration:

$$\begin{aligned} Q = K_{sp} = [Ca^{2+}]\,[C_2O_4^{2-}] &= 1.96 \times 10^{-9} \\ (2.2 \times 10^{-3})\,[C_2O_4^{2-}] &= 1.96 \times 10^{-9} \\ [C_2O_4^{2-}] &= \frac{1.96 \times 10^{-9}}{2.2 \times 10^{-3}} \\ &= 8.9 \times 10^{-7}\ \text{M} \end{aligned} \qquad (15.2.1)$$

A concentration of $[C_2O_4^{2-}] = 8.9 \times 10^{-7}$ M is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 15.2.9

If a solution contains 0.0020 mol of $\mathrm{CrO_4^{2-}}$ per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer

$6.7\time10^{-5}\ \mathrm{M}$

Example 15.2.10: Concentrations Following Precipitation

Clothing washed in water that has a manganese $[\mathrm{Mn^{2+}(aq)}]$ concentration exceeding 0.1 mg/L (1.8×10^{-6} M) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be decreased by adding a base to precipitate $Mn(OH)_2$. What pH is required to keep $[Mn^{2+}]$ equal to 1.8×10^{-6} M?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2\,(s) \rightleftharpoons Mn^{2+}\,(aq) + 2\,OH^-\,(aq)} \qquad K_{sp} = 2 \times 10^{-13}$$

At equilibrium:

$$K_{sp} = \left[\mathrm{Mn^{2+}}\right]\left[\mathrm{OH^-}\right]^2$$

or

$$\left(1.8 \times 10^{-6}\right)\left[\mathrm{OH^-}\right]^2 = 2 \times 10^{-13}$$

so

$$\left[\mathrm{OH^-}\right] = 3.3 \times 10^{-4} M$$

Calculate the pH from the pOH:

$$\begin{aligned}\mathrm{pOH} &= -\log\left[\mathrm{OH^-}\right] \\ &= -\log(3.3 \times 10^{-4}) = 3.48 \\ \mathrm{pH} &= 14.00 - \mathrm{pOH} \\ &= 14.00 - 3.48 \\ &= 10.52\end{aligned}$$

(final result rounded to one significant digit, limited by the certainty of the K_{sp})

Exercise 15.2.10

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} M. Calculate the pH at which $[Mg^{2+}]$ is decreased to 1.0×10^{-5} M

Answer

10.97

In solutions containing two or more ions that may form insoluble compounds with the same counter ion, an experimental strategy called selective precipitation may be used to remove individual ions from solution. By increasing the counter ion concentration in a controlled manner, ions in solution may be precipitated individually, assuming their compound solubilities are adequately different. In solutions with equal concentrations of target ions, the ion forming the least soluble compound will precipitate first (at the lowest concentration of counter ion), with the other ions subsequently precipitating as their compound's solubilities are reached. As an

illustration of this technique, the next example exercise describes separation of a two halide ions via precipitation of one as a silver salt.

Chemistry in Everyday Life: The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure **15.2.5**). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.



Figure **15.2.5**: Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, or lime, $Ca(OH)_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3OH$, which then precipitates out of the solution:

$$5\,Ca^{2+} + 3\,PO_4{}^{3-} + OH^- \rightleftharpoons Ca_5\,(PO_4)_3\,\cdot OH\,(s)$$

Because the amount of calcium ion added does not result in exceeding the solubility products for other calcium salts, the anions of those salts remain behind in the wastewater. The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this site for more information on how phosphorus is removed from wastewater.

Example 15.2.11: Precipitation of Silver Halides

A solution contains 0.00010 mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

Solution

The two equilibria involved are:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$
$$AgBr\,(s) \rightleftharpoons Ag^+\,(aq) + Br^-\,(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$$

If the solution contained about *equal* concentrations of Cl^- and Br^-, then the silver salt with the smaller K_{sp} (AgBr) would precipitate first. The concentrations are not equal, however, so the $[Ag^+]$ at which AgCl begins to precipitate and the $[Ag^+]$ at which AgBr begins to precipitate must be calculated. The salt that forms at the lower $[Ag^+]$ precipitates first.

AgBr precipitates when Q equals K_{sp} for AgBr

$$Q_{sp} = K_{sp} = [Ag^+]\,[Br^-] = [Ag^+]\,(0.00010) = 5.0 \times 10^{-13}$$

$$[Ag^+] = \frac{5.0 \times 10^{-13}}{0.00010}$$

$$= 5.0 \times 10^{-9}\ M$$

AgBr begins to precipitate when $[Ag^+]$ is 5.0×10^{-9} M.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10^{-10}). When $[Cl^-]$ = 0.10 M:

$$Q_{sp} = K_{sp} = [Ag^+]\,[Cl^-] = [Ag^+]\,(0.10) = 1.6 \times 10^{-10}$$

$$[Ag^+] = \frac{1.6 \times 10^{-10}}{0.10}$$

$$= 1.6 \times 10^{-9}\ M$$

AgCl begins to precipitate when $[Ag^+]$ is 1.6×10^{-9} M.

AgCl begins to precipitate at a lower $[Ag^+]$ than AgBr, so AgCl begins to precipitate first. Note the chloride ion concentration of the initial mixture was significantly greater than the bromide ion concentration, and so silver chloride precipitated first despite having a K_{sp} greater than that of silver bromide.

? Exercise 15.2.11

If silver nitrate solution is added to a solution which is 0.050 M in both Cl^- and Br^- ions, at what $[Ag^+]$ would precipitation begin, and what would be the formula of the precipitate?

Answer

$[Ag^+] = 1.0 \times 10^{-11}$ M; **AgBr** precipitates first

Common Ion Effect

Compared with pure water, the solubility of an ionic compound is less in aqueous solutions containing a *common ion* (one also produced by dissolution of the ionic compound). This is an example of a phenomenon known as the **common ion effect**, which is a consequence of the law of mass action that may be explained using Le Chatelier's principle. Consider the dissolution of silver iodide:

$$AgI\,(s) \rightleftharpoons Ag^+\,(aq) + I^-\,(aq)$$

This solubility equilibrium may be shifted left by the addition of either silver(I) or iodide ions, resulting in the precipitation of AgI and lowered concentrations of dissolved Ag^+ and I^-. In solutions that already contain either of these ions, less AgI may be dissolved than in solutions without these ions.

This effect may also be explained in terms of mass action as represented in the solubility product expression:

$$K_{sp} = [Ag^+]\,[I^-]$$

The mathematical product of silver(I) and iodide ion molarities is constant in an equilibrium mixture *regardless of the source of the ions*, and so an increase in one ion's concentration must be balanced by a proportional decrease in the other.

Link to Learning

View this simulation to explore various aspects of the common ion effect.

Example 15.2.12: Common Ion Effect on Solubility

What is the effect on the amount of solid $Mg(OH)_2$ and the concentrations of Mg^{2+} and OH^- when each of the following are added to a saturated solution of $Mg(OH)_2$?

a. $MgCl_2$
b. KOH
c. $NaNO_3$
d. $Mg(OH)_2$

Solution

The solubility equilibrium is

$$\mathrm{Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

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 no effect on the magnesium hydroxide solubility equilibrium is expected.
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.

Exercise 15.2.12

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. $Ni(NO_3)_2$
b. $KClO_4$
c. $NiCO_3$
d. K_2CO_3

Answer

(a) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ increases, $\mathrm{CO_3^{2-}}$ decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid $NiCO_3$; (d) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ decreases, $\mathrm{CO_3^{2-}}$ increases;

Example 15.2.13: 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 $\mathrm{1.0 \times 10^{-28}}$.

Solution

This calculation can be performed using the ICE approach:

$$\mathrm{CdS\,(s) \rightleftharpoons Cd^{2+}\,(aq) + S^{2-}\,(aq)}$$

	$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$		
Initial concentration (*M*)		0.010	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		$0.010 + x$	x

$$K_{sp} = [Cd^{2+}][S^{2-}] = 1.0 \times 10^{-28}$$
$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

Because Ksp is very small, assume $x \ll 0.010$ and solve the simplified equation for x:

$$(0.010)(x) = 1.0 \times 10^{-28}$$
$$x = 1.0 \times 10^{-26}\ \text{M}$$

The molar solubility of CdS in this solution is 1.0×10^{-26} M.

? Exercise 15.2.13

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

4×10^{-11} M

This page titled 15.2: Precipitation and Dissolution is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **15.1: Precipitation and Dissolution** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

15.3: Lewis Acids and Bases

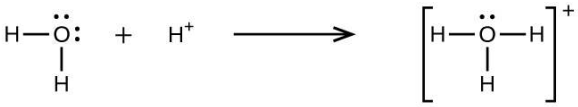
Learning Objectives

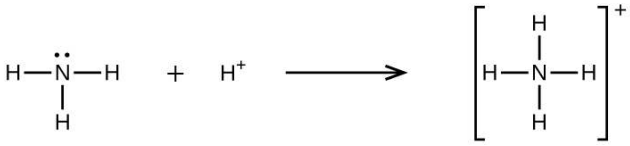
By the end of this section, you will be able to:

- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

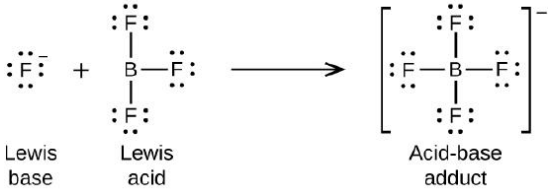
A **coordinate covalent bond** (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.



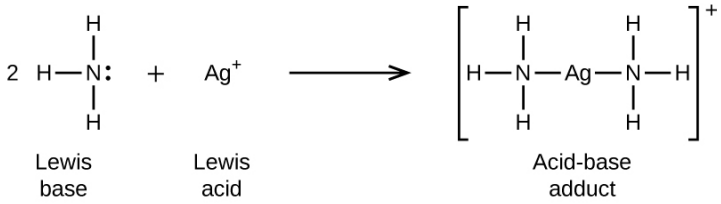


Reactions involving the formation of coordinate covalent bonds are classified as **Lewis acid-base chemistry**. The species donating the electron pair that compose the bond is a **Lewis base**, the species accepting the electron pair is a **Lewis acid**, and the product of the reaction is a **Lewis acid-base adduct**. 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^+. A few examples involving other Lewis acids and bases are described below.

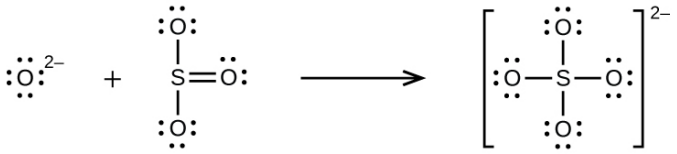
The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



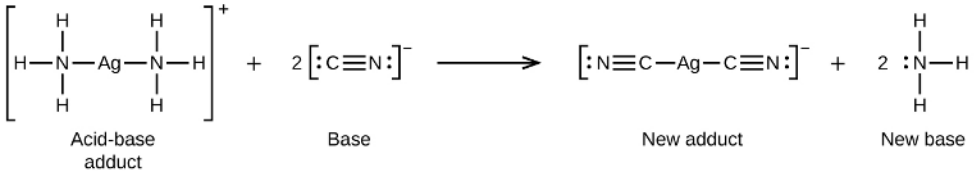
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:

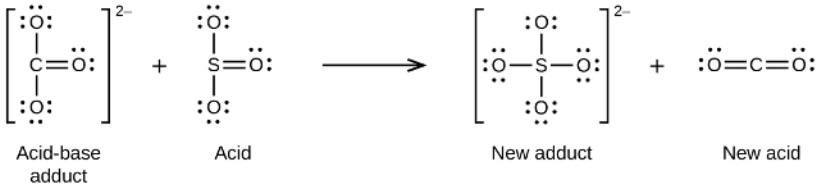


Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:



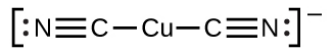
Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:





Another type of Lewis acid-base chemistry involves the formation of a complex ion (or a coordination complex) comprising a central atom, typically a transition metal cation, surrounded by ions or molecules called **ligands**. These ligands can be neutral molecules like H_2O or NH_3, or ions such as CN^- or OH^-. Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. These types of Lewis acid-base reactions are examples of a broad subdiscipline called *coordination chemistry*—the topic of another chapter in this text.

The equilibrium constant for the reaction of a metal ion with one or more ligands to form a coordination complex is called a **formation constant** (K_f) (sometimes called a stability constant). For example, the complex ion



is produced by the reaction

$$\mathrm{Cu^+(aq) + 2\,CN^-(aq) \rightleftharpoons Cu(CN)_2{}^-(aq)}$$

The formation constant for this reaction is

$$K_f = \frac{[\mathrm{Cu(CN)_2{}^-}]}{[\mathrm{Cu^+}]\,[\mathrm{CN^-}]^2}$$

Alternatively, the reverse reaction (decomposition of the complex ion) can be considered, in which case the equilibrium constant is a dissociation constant (K_d). Per the relation between equilibrium constants for reciprocal reactions described, the dissociation constant is the mathematical inverse of the formation constant, $K_d = K_f^{-1}$. A tabulation of formation constants is provided in Appendix K.

As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[\mathrm{Ag^+}] = 1.3 \times 10^{-5}$ M):

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)}$$

However, if NH_3 is present in the water, the complex ion, $\mathrm{Ag(NH_3)_2{}^+}$ can form according to the equation:

$$\mathrm{Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)}$$

with

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$$

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of AgCl combine with NH_3 to form $Ag(NH_3)_2^+$. As a consequence, the concentration of silver ions, $[Ag^+]$, is reduced, and the reaction quotient for the dissolution of silver chloride, $[Ag^+][Cl^-]$, falls below the solubility product of AgCl:

$$Q = [Ag^+]\,[Cl^-] < K_{sp}$$

More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

Example 15.3.1: Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 *M* with respect to $Ag(NH_3)_2^+$).

Solution

Applying the standard ICE approach to this reaction yields the following:

	$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$		
Initial concentration (*M*)	0	0	0.10
Change (*M*)	$+x$	$+2x$	$-x$
Equilibrium concentration (*M*)	x	$2x$	$0.10 - x$

Substituting these equilibrium concentration terms into the K_f expression gives

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2}$$

The very large equilibrium constant means the amount of the complex ion that will dissociate, x, will be very small. Assuming $x \ll 0.1$ permits simplifying the above equation:

$$1.7 \times 10^7 = \frac{0.10}{(x)(2x)^2}$$

$$x^3 = \frac{0.10}{4\left(1.7 \times 10^7\right)} = 1.5 \times 10^{-9}$$

$$x = \sqrt[3]{1.5 \times 10^{-9}} = 1.1 \times 10^{-3}$$

Because only 1.1% of the $Ag(NH_3)_2^+$) dissociates into Ag^+ and NH_3, the assumption that x is small is justified.

Using this value of x and the relations in the above ICE table allows calculation of all species' equilibrium concentrations:

$$[Ag^+] = 0 + x = 1.1 \times 10^{-3}\ \text{M}$$

$$[NH_3] = 0 + 2x = 2.2 \times 10^{-3}\ \text{M}$$

$$[Ag(NH_3)_2^+] = 0.10 - x = 0.10 - 0.0011$$

$$= 0.099\ \text{M}$$

The concentration of free silver ion in the solution is 0.0011 *M*.

Exercise 15.3.1

Calculate the silver ion concentration, $[Ag^+]$, of a solution prepared by dissolving 1.00 g of $AgNO_3$ and 10.0 g of KCN in sufficient water to make 1.00 L of solution. (Hint: Because K_f is very large, assume the reaction goes to completion then calculate the $[Ag^+]$ produced by dissociation of the complex.)

Answer

2.9×10^{-22} M

This page titled 15.3: Lewis Acids and Bases is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **15.2: Lewis Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

15.4: Coupled Equilibria

Learning Objectives

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

- Describe examples of systems involving two (or more) coupled chemical equilibria
- Calculate reactant and product concentrations for coupled equilibrium systems

As discussed in preceding chapters on equilibrium, *coupled equilibria* involve two or more separate chemical reactions that share one or more reactants or products. This section of this chapter will address solubility equilibria coupled with acid-base and complex-formation reactions.

An environmentally relevant example illustrating the coupling of solubility and acid-base equilibria is the impact of ocean acidification on the health of the ocean's coral reefs. These reefs are built upon skeletons of sparingly soluble calcium carbonate excreted by colonies of corals (small marine invertebrates). The relevant dissolution equilibrium is

$$\mathrm{CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3{}^{-2}\,(aq)} \quad K_{sp} = 8.7 \times 10^{-9}$$

Rising concentrations of atmospheric carbon dioxide contribute to an increased acidity of ocean waters due to the dissolution, hydrolysis, and acid ionization of carbon dioxide:

$$\mathrm{CO_2\,(g) \rightleftharpoons CO_2\,(aq)}$$

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2\,CO_3\,(aq)}$$

$$\mathrm{H_2\,CO_3\,(aq) + H_2O\,(l) \rightleftharpoons HCO_3{}^{-}\,(aq) + H_3O^{+}\,(aq)} \quad K_{a1} = 4.3 \times 10^{-7}$$

$$\mathrm{HCO_3{}^{-}\,(aq) + H_2O\,(l) \rightleftharpoons CO_3{}^{2-}\,(aq) + H_3O^{+}\,(aq)} \quad K_{a2} = 4.7 \times 10^{-11}$$

Inspection of these equilibria shows the carbonate ion is involved in the calcium carbonate dissolution and the acid hydrolysis of bicarbonate ion. Combining the dissolution equation with the reverse of the acid hydrolysis equation yields

$$\mathrm{CaCO_3\,(s) + H_3O^{+}\,(aq) \rightleftharpoons Ca^{2+}\,(aq) + HCO_3{}^{-}\,(aq) + H_2O\,(l)} \qquad K = K_{sp}\,/K_{a2} = 180$$

The equilibrium constant for this net reaction is much greater than the K_{sp} for calcium carbonate, indicating its solubility is markedly increased in acidic solutions. As rising carbon dioxide levels in the atmosphere increase the acidity of ocean waters, the calcium carbonate skeletons of coral reefs become more prone to dissolution and subsequently less healthy (Figure **15.4.1**).

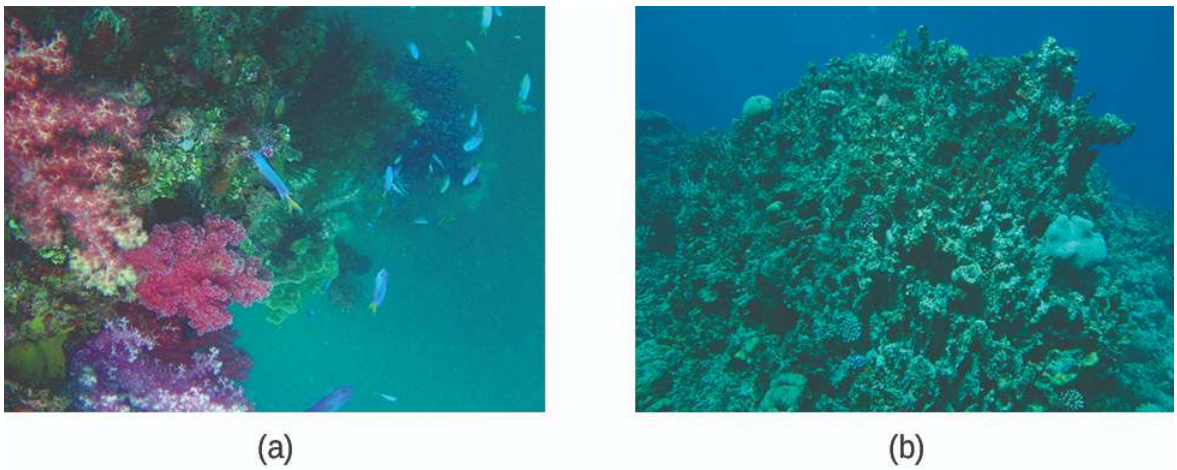


Figure **15.4.1**: Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonate skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library; credit b: modification of work by "prilfish"/Flickr)

Link to Learning

Learn more about ocean acidification and how it affects other marine creatures.

This site has detailed information about how ocean acidification specifically affects coral reefs.

The dramatic increase in solubility with increasing acidity described above for calcium carbonate is typical of salts containing basic anions (e.g., carbonate, fluoride, hydroxide, sulfide). Another familiar example is the formation of dental cavities in tooth enamel. The major mineral component of enamel is calcium hydroxyapatite (Figure **15.4.2**), a sparingly soluble ionic compound whose dissolution equilibrium is

$$Ca_5(PO_4)_3OH\,(s) \rightleftharpoons 5\,Ca^{2+}\,(aq) + 3\,PO_4{}^{3-}\,(aq) + OH^-\,(aq)$$



Figure **15.4.2**: Crystal of the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$, is shown here. The pure compound is white, but like many other minerals, this sample is colored because of the presence of impurities.

This compound dissolved to yield two different basic ions: triprotic phosphate ions

$$PO_4{}^{3-}\,(aq) + H_3O^+\,(aq) \longrightarrow H_2\,PO_4{}^{2-}\,(aq) + H_2O\,(l)$$
$$H_2\,PO_4{}^{2-}\,(aq) + H_3O^+\,(aq) \longrightarrow H_2\,PO_4{}^-\,(aq) + H_2O\,(l)$$
$$H_2\,PO_4{}^-\,(aq) + H_3O^+\,(aq) \longrightarrow H_3\,PO_4\,(aq) + H_2O\,(l)$$

and monoprotic hydroxide ions:

$$OH^-\,(aq) + H_3O^+ \longrightarrow 2\,H_2O$$

Of the two basic productions, the hydroxide is, of course, by far the stronger base (it's the strongest base that can exist in aqueous solution), and so it is the dominant factor providing the compound an acid-dependent solubility. Dental cavities form when the acid waste of bacteria growing on the surface of teeth hastens the dissolution of tooth enamel by reacting completely with the strong base hydroxide, shifting the hydroxyapatite solubility equilibrium to the right. Some toothpastes and mouth rinses contain added NaF or SnF_2 that make enamel more acid resistant by replacing the strong base hydroxide with the weak base fluoride:

$$NaF + Ca_5(PO_4)_3OH \rightleftharpoons Ca_5(PO_4)_3F + Na^+ + OH^-$$

The weak base fluoride ion reacts only partially with the bacterial acid waste, resulting in a less extensive shift in the solubility equilibrium and an increased resistance to acid dissolution. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Chemistry in Everyday Life: Role of Fluoride in Preventing Tooth Decay

As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $Ca_5(PO_4)_3F$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became

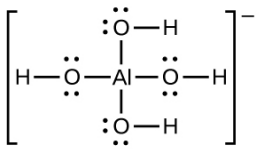
common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (Figure 15.4.3).



Figure 15.4.3: Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

The solubility of ionic compounds may also be increased when dissolution is coupled to the formation of a complex ion. For example, aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion



The equations for the dissolution of aluminum hydroxide, the formation of the complex ion, and the combined (net) equation are shown below. As indicated by the relatively large value of K for the net reaction, coupling complex formation with dissolution drastically increases the solubility of $Al(OH)_3$.

$$\mathrm{Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)} \qquad K_{sp} = 2 \times 10^{-32}$$

$$\mathrm{Al^{3+}(aq) + 4\,OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)} \qquad K_f = 1.1 \times 10^{33}$$

$$\mathrm{Net:\ Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)} \qquad K = K_{sp}K_f = 22$$

Example 15.4.1: Increased Solubility in Acidic Solutions

Compute and compare the molar solubilities for aluminum hydroxide, $Al(OH)_3$, dissolved in (a) pure water and (b) a buffer containing 0.100 *M* acetic acid and 0.100 *M* sodium acetate.

Solution

(a) The molar solubility of aluminum hydroxide in water is computed considering the dissolution equilibrium only as demonstrated in several previous examples:

\[\ce{Al(OH)_3(s) <=> Al^{3+}(aq) +3 OH^{-}(aq)} \quad \quad K_{ sp }=2 \times 10^{-32} \nonumber]

$$\text{molar solubility in water} = [Al^{3+}] = \left(\frac{2 \times 10^{-32}}{27}\right)^{1/4} = 5 \times 10^{-9}\ \text{M}$$

(b) The concentration of hydroxide ion of the buffered solution is conveniently calculated by the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
$$= 4.74 + \log\left(\frac{0.100}{0.100}\right) = 4.74$$

At this pH, the concentration of hydroxide ion is

$$\text{pOH} = 14.00 - 4.74 = 9.26$$
$$[\text{OH}^-] = 10^{-9.26} = 5.5 \times 10^{-10}$$

The solubility of Al(OH)_3 in this buffer is then calculated from its solubility product expression:

$$K_{sp} = [\text{Al}^{3+}]\,[\text{OH}^-]^3$$

Via

$$\begin{aligned}\text{molar solubility in buffer} &= [\text{Al}^{3+}] \\ &= \frac{K_{sp}}{[\text{OH}^-]^3} \\ &= \frac{2 \times 10^{-32}}{(5.5 \times 10^{-10})^3} \\ &= 1.2 \times 10^{-4}\ \text{M}\end{aligned}$$

Compared to pure water, the solubility of aluminum hydroxide in this mildly acidic buffer is approximately ten million times greater (though still relatively low).

Exercise 15.4.1

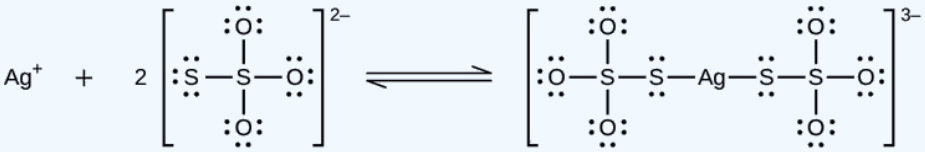
What is the solubility of aluminum hydroxide in a buffer comprised of 0.100 *M* formic acid and 0.100 *M* sodium formate?

Answer

0.1 *M*

Example 15.4.2: Multiple Equilibria

Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, called hypo) to form the complex ion $\text{Ag(S}_2\text{O}_3)_2^{3-}$ with $K_f = 4.7 \times 10^{13}$.



What mass of $\text{Na}_2\text{S}_2\text{O}_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $\text{Ag(S}_2\text{O}_3)_2^{3-}$

Solution

Two equilibria are involved when silver bromide dissolves in an aqueous thiosulfate solution containing the ion:

- **dissolution**:

$$\text{AgBr}\,(s) \rightleftharpoons \text{Ag}^+\,(aq) + \text{Br}^-\,(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$$

- **complexation**:

$$\text{Ag}^+\,(aq) + 2\,\text{S}_2\text{O}_3{}^{2-}\,(aq) \rightleftharpoons \text{Ag}\,(\,\text{S}_2\text{O}_3)_2{}^{3-}\,(aq) \qquad K_f = 4.7 \times 10^{13}$$

Combining these two equilibrium equations yields

$$\mathrm{AgBr\,(s) + 2\,S_2O_3^{2-}\,(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}\,(aq) + Br^-\,(aq)}$$

with

$$K = \frac{[\mathrm{Ag(S_2O_3)_2}^3]\,[\mathrm{Br^-}]}{[\mathrm{S_2O_3}^{-2}]^2} = K_{sp}K_f = 24$$

The concentration of bromide resulting from dissolution of 1.00 g of AgBr in 1.00 L of solution is

$$[Br^-] = \frac{1.00\text{ g AgBr} \times \frac{1\text{ mol AgBr}}{187.77\text{ g / mol}} \times \frac{1\text{ mol Br}^-}{1\text{ mol AgBr}^-}}{1.00\text{ L}} = 0.00532\text{ M}$$

The stoichiometry of the dissolution equilibrium indicates the same concentration of aqueous silver ion will result, 0.00532 M, and the very large value of ensures that essentially all the dissolved silver ion will be complexed by thiosulfate ion:

$$[\mathrm{Ag(S_2O_3)_2}^{3-}] = 0.00532\text{ M}$$

Rearranging the K expression for the combined equilibrium equations and solving for the concentration of thiosulfate ion yields

$$[\mathrm{S_2O_3}^{2-}] = \frac{[\mathrm{Ag(S_2O_3)_2}^{3-}]\,[\mathrm{Br^-}]}{K} = \frac{(0.00532M)(0.00532\text{ M})}{24} = 0.0011\text{ M}$$

Finally, the total mass of $\mathrm{Na_2S_2O_3}$ required to provide enough thiosulfate to yield the concentrations cited above can be calculated.

Mass of $\mathrm{Na_2S_2O_3}$ required to yield 0.00532 M $\mathrm{Ag(2\,S_2O_3)_2}^{3-}$

$$0.00532\frac{\text{mol Ag(S}_2\text{O}_3)_2^{3-}}{1.00\text{ L}} \times \frac{2\text{ mol S}_2\text{O}_3^{2-}}{1\text{ mol Ag(S}_2\text{O}_3)_2^{3-}} \times \frac{1\text{ mol Na}_2\text{S}_2\text{O}_3}{1\text{ mol S}_2\text{O}_3^{2-}} \times \frac{158.1\text{ g Na}_2\text{S}_2\text{O}_3}{1\text{ mol Na}_2\text{S}_2\text{O}_3} = 1.68\text{ g}$$

Mass of $\mathrm{Na_2S_2O_3}$ required to yield 0.00110 M $\mathrm{S_2O_3}^{2-}$

$$0.0011\frac{\text{mol S}_2\text{O}_3^{2-}}{1.00\text{ L}} \times \frac{1\text{ mol S}_2\text{O}_3^{2-}}{1\text{ mol Na}_2\text{S}_2\text{O}_3} \times \frac{158.1\text{ g Na}_2\text{S}_2\text{O}_3}{1\text{ mol Na}_2\text{S}_2\text{O}_3} = 0.17\text{ g}$$

The mass of required to dissolve 1.00 g of AgBr in 1.00 L of water is thus 1.68 g + 0.17 g = 1.85 g

? Exercise 15.4.2

AgCl(*s*), silver chloride, has a very low solubility:

$$\mathrm{AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)} \qquad K_{so} = 1.6 \times 10^{-10}$$

Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed:

$$\mathrm{Ag^+\,(aq) + 2\,NH_3\,(aq) \rightleftharpoons Ag(NH_3)_2^+\,(aq)} \qquad K_f = 1.7 \times 10^7$$

What mass of $\mathrm{NH_3}$ is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $\mathrm{Ag(NH_3)^{2+}}$?

Answer

1.00 L of a solution prepared with 4.81 g NH_3 dissolves 2.0 g of AgCl.

This page titled 15.4: Coupled Equilibria is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **15.3: Coupled Equilibria** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

15.5: Key Terms

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

complex ion | ion consisting of a central atom surrounding molecules or ions called ligands via coordinate covalent bonds

coordinate covalent bond | (also, dative bond) covalent bond in which both electrons originated from the same atom

coupled equilibria | system characterized the simultaneous establishment of two or more equilibrium reactions sharing one or more reactant or product

dissociation constant | (K_d) equilibrium constant for the decomposition of a complex ion into its components

formation constant | (K_f) (also, stability constant) equilibrium constant for the formation of a complex ion from its components

Lewis acid | any species that can accept a pair of electrons and form a coordinate covalent bond

Lewis acid-base adduct | compound or ion that contains a coordinate covalent bond between a Lewis acid and a Lewis base

Lewis acid-base chemistry | reactions involving the formation of coordinate covalent bonds

Lewis base | any species that can donate a pair of electrons and form a coordinate covalent bond

ligand | molecule or ion acting as a Lewis base in complex ion formation; bonds to the central atom of the complex

molar solubility | solubility of a compound expressed in units of moles per liter (mol/L)

selective precipitation | process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product constant (K_{sp}) | equilibrium constant for the dissolution of an ionic compound

15.5: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **15.4: Key Terms** is licensed CC BY 4.0.

15.6: Key Equations

15.6: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **15.5: Key Equations** is licensed CC BY 4.0.

15.7: Summary

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp}, of the solid. For a heterogeneous equilibrium involving the slightly soluble solid M_pX_q and its ions M^{m+} and X^{n-}:

the solubility product expression is:

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp}, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions.

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product.

A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts and comprise central metal atoms or ions acting as Lewis acids bonded to molecules or ions called ligands that act as Lewis bases. The equilibrium constant for the reaction between a metal ion and ligands produces a complex ion called a formation constant; for the reverse reaction, it is called a dissociation constant.

Systems involving two or more chemical equilibria that share one or more reactant or product are called coupled equilibria. Common examples of coupled equilibria include the increased solubility of some compounds in acidic solutions (coupled dissolution and neutralization equilibria) and in solutions containing ligands (coupled dissolution and complex formation). The equilibrium tools from other chapters may be applied to describe and perform calculations on these systems.

15.7: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **15.6: Summary** is licensed CC BY 4.0.

15.8: Exercises

1.

Complete the changes in concentrations for each of the following reactions:

(a)

(b)

(c)

(d)

(e)

2.

Complete the changes in concentrations for each of the following reactions:

(a)

(b

(c)

(d)

(e)

3.

How do the concentrations of Ag^+ and in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain.

4.

How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS?

5.

What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised?

6.

Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: $CoSO_3$, CuI, $PbCO_3$, $PbCl_2$, Tl_2S, $KClO_4$?

7.

Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl, $BaSO_4$, CaF_2, Hg_2I_2, $MnCO_3$, and ZnS?

8.

Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:

a. $PbCl_2$
b. Ag_2S
c. $Sr_3(PO_4)_2$
d. $SrSO_4$

9.

Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

a. LaF_3
b. $CaCO_3$

c. Ag_2SO_4
d. $Pb(OH)_2$

10.

The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

a. $BaSiF_6$, 0.026 g/100 mL (contains ions)
b. $Ce(IO_3)_4$, 1.5 10^{-2} g/100 mL
c. $Gd_2(SO_4)_3$, 3.98 g/100 mL
d. $(NH_4)_2PtBr_6$, 0.59 g/100 mL (contains ions)

11.

The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

a. $BaSeO_4$, 0.0118 g/100 mL
b. $Ba(BrO_3)_2 \cdot H_2O$, 0.30 g/100 mL
c. $NH_4MgAsO_4 \cdot 6H_2O$, 0.038 g/100 mL
d. $La_2(MoO_4)_3$, 0.00179 g/100 mL

12.

Use solubility products and predict which of the following salts is the most soluble, in terms of moles per liter, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.

13.

Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

a. $KHC_4H_4O_6$
b. PbI_2
c. $Ag_4[Fe(CN)_6]$, a salt containing the ion
d. Hg_2I_2

14.

Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

a. Ag_2SO_4
b. $PbBr_2$
c. AgI
d. $CaC_2O_4 \cdot H_2O$

15.

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

a. AgCl(*s*) in 0.025 *M* NaCl
b. CaF_2(*s*) in 0.00133 *M* KF
c. Ag_2SO_4(*s*) in 0.500 L of a solution containing 19.50 g of K_2SO_4
d. $Zn(OH)_2$(*s*) in a solution buffered at a pH of 11.45

16.

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

a. $TlCl(s)$ in 1.250 *M* HCl
b. $PbI_2(s)$ in 0.0355 *M* CaI_2
c. $Ag_2CrO_4(s)$ in 0.225 L of a solution containing 0.856 g of K_2CrO_4
d. $Cd(OH)_2(s)$ in a solution buffered at a pH of 10.995

17.

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.

a. $TlCl(s)$ in 0.025 *M* $TlNO_3$
b. $BaF_2(s)$ in 0.0313 *M* KF
c. MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $Mg(NO_3)_2$
d. $Ca(OH)_2(s)$ in an unbuffered solution initially with a pH of 12.700

18.

Explain why the changes in concentrations of the common ions in Exercise 15.17 can be neglected.

19.

Explain why the changes in concentrations of the common ions in Exercise 15.18 cannot be neglected.

20.

Calculate the solubility of aluminum hydroxide, $Al(OH)_3$, in a solution buffered at pH 11.00.

21.

Refer to Appendix J for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per liter and which is most soluble in grams per liter.

22.

Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract (Figure 15.4). This use of $BaSO_4$ is possible because of its low solubility. Calculate the molar solubility of $BaSO_4$ and the mass of barium present in 1.00 L of water saturated with $BaSO_4$.

23.

Public Health Service standards for drinking water set a maximum of 250 mg/L ($2.60\ 10^{-3}$ *M*) of because of its cathartic action (it is a laxative). Does natural water that is saturated with $CaSO_4$ (“gyp” water) as a result or passing through soil containing gypsum, $CaSO_4{\cdot}2H_2O$, meet these standards? What is the concentration of in such water?

24.

Perform the following calculations:

a. Calculate $[Ag^+]$ in a saturated aqueous solution of AgBr.
b. What will $[Ag^+]$ be when enough KBr has been added to make $[Br^-] = 0.050$ *M*?
c. What will $[Br^-]$ be when enough $AgNO_3$ has been added to make $[Ag^+] = 0.020$ *M*?

25.

The solubility product of $CaSO_4{\cdot}2H_2O$ is $2.4\ 10^{-5}$. What mass of this salt will dissolve in 1.0 L of 0.010 *M*

26.

Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Appendix J for solubility products).

a. TlCl

b. BaF_2
c. Ag_2CrO_4
d. $CaC_2O_4 \cdot H_2O$
e. the mineral anglesite, $PbSO_4$

27.

Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Appendix J for solubility products):

a. AgI
b. Ag_2SO_4
c. $Mn(OH)_2$
d. $Sr(OH)_2 \cdot 8H_2O$
e. the mineral brucite, $Mg(OH)_2$

28.

The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

a. AgBr: $[Ag^+] = 5.7\ 10^{-7}\ M$, $[Br^-] = 5.7\ 10^{-7}\ M$
b. $CaCO_3$: $[Ca^{2+}] = 5.3\ 10^{-3}\ M$, $= 9.0\ 10^{-7}\ M$
c. PbF_2: $[Pb^{2+}] = 2.1\ 10^{-3}\ M$, $[F^-] = 4.2\ 10^{-3}\ M$
d. Ag_2CrO_4: $[Ag^+] = 5.3\ 10^{-5}\ M$, $3.2\ 10^{-3}\ M$
e. InF_3: $[In^{3+}] = 2.3\ 10^{-3}\ M$, $[F^-] = 7.0\ 10^{-3}\ M$

29.

The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

a. TlCl: $[Tl^+] = 1.21\ 10^{-2}\ M$, $[Cl^-] = 1.2\ 10^{-2}\ M$
b. $Ce(IO_3)_4$: $[Ce^{4+}] = 1.8\ 10^{-4}\ M$, $= 2.6\ 10^{-13}\ M$
c. $Gd_2(SO_4)_3$: $[Gd^{3+}] = 0.132\ M$, $= 0.198\ M$
d. Ag_2SO_4: $[Ag^+] = 2.40\ 10^{-2}\ M$, $= 2.05\ 10^{-2}\ M$
e. $BaSO_4$: $[Ba^{2+}] = 0.500\ M$, $= 4.6\ 10^{-8}\ M$

30.

Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Appendix J for K_{sp} values.)

a. $KClO_4$: $[K^+] = 0.01\ M$, $= 0.01\ M$
b. K_2PtCl_6: $[K^+] = 0.01\ M$, $= 0.01\ M$
c. PbI_2: $[Pb^{2+}] = 0.003\ M$, $[I^-] = 1.3\ 10^{-3}\ M$
d. Ag_2S: $[Ag^+] = 1\ 10^{-10}\ M$, $[S^{2-}] = 1\ 10^{-13}\ M$

31.

Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Appendix J for K_{sp} values.)

a. $CaCO_3$: $[Ca^{2+}] = 0.003\ M$, $= 0.003\ M$
b. $Co(OH)_2$: $[Co^{2+}] = 0.01\ M$, $[OH^-] = 1\ 10^{-7}\ M$
c. $CaHPO_4$: $[Ca^{2+}] = 0.01\ M$, $= 2\ 10^{-6}\ M$
d. $Pb_3(PO_4)_2$: $[Pb^{2+}] = 0.01\ M$, $= 1\ 10^{-13}\ M$

32.

Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 M in Cl^-.

33.

Calculate the concentration of sulfate ion when $BaSO_4$ just begins to precipitate from a solution that is 0.0758 *M* in Ba^{2+}.

34.

Calculate the concentration of Sr^{2+} when $SrCrO_4$ starts to precipitate from a solution that is 0.0025 *M* in CrO_4^{2-}.

35.

Calculate the concentration of when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 *M* in Ag^+.

36.

Calculate the concentration of F^- required to begin precipitation of CaF_2 in a solution that is 0.010 *M* in Ca^{2+}.

37.

Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is $2.50\ 10^{-6}$ *M* in

38.

What $[Ag^+]$ is required to reduce to $8.2\ 10^{-4}$ *M* by precipitation of Ag_2CO_3?

39.

What $[F^-]$ is required to reduce $[Ca^{2+}]$ to $1.0\ 10^{-4}$ *M* by precipitation of CaF_2?

40.

A volume of 0.800 L of a $2\ 10^{-4}$-*M* $Ba(NO_3)_2$ solution is added to 0.200 L of $5\ 10^{-4}$ *M* Li_2SO_4. Does $BaSO_4$ precipitate? Explain your answer.

41.

Perform these calculations for nickel(II) carbonate. (a) With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ ($K_{sp} = 1.36\ 10^{-7}$).

(b) If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ ($K_{sp} = 1.0\ 10^{-12}$), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.

42.

Iron concentrations greater than $5.4\ 10^{-6}$ *M* in water used for laundry purposes can cause staining. What $[OH^-]$ is required to reduce $[Fe^{2+}]$ to this level by precipitation of $Fe(OH)_2$?

43.

A solution is 0.010 *M* in both Cu^{2+} and Cd^{2+}. What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide?

44.

A solution is 0.15 *M* in both Pb^{2+} and Ag^+. If Cl^- is added to this solution, what is $[Ag^+]$ when $PbCl_2$ begins to precipitate?

45.

What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 *M* with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in Appendix J.)

a. (f) and OH^-

46.

A solution contains $1.0\ 10^{-5}$ mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

47.

A solution contains $1.0\ 10^{-2}$ mol of KI and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

48.

The calcium ions in human blood serum are necessary for coagulation (Figure 15.5). Potassium oxalate, $K_2C_2O_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $CaC_2O_4·H_2O$. It is necessary to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $K_2C_2O_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)

49.

About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form?

50.

The pH of normal urine is 6.30, and the total phosphate concentration

51.

Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $Mg^{2+}(aq)$ by mass. What mass, in kilograms, of $Ca(OH)_2$ is required to precipitate 99.9% of the magnesium in 1.00 10^3 L of sea water?

52.

Hydrogen sulfide is bubbled into a solution that is 0.10 *M* in both Pb^{2+} and Fe^{2+} and 0.30 *M* in HCl. After the solution has come to equilibrium it is saturated with H_2S ($[H_2S] = 0.10$ *M*). What concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H_2S we can use the equilibrium:

(Hint: The changes as metal sulfides precipitate.)

53.

Perform the following calculations involving concentrations of iodate ions:

a. The iodate ion concentration of a saturated solution of $La(IO_3)_3$ was found to be 3.1 10^{-3} mol/L. Find the K_{sp}.
b. Find the concentration of iodate ions in a saturated solution of $Cu(IO_3)_2$ (K_{sp} = 7.4 10^{-8}).

54.

Calculate the molar solubility of AgBr in 0.035 *M* NaBr (K_{sp} = 5 10^{-13}).

55.

How many grams of $Pb(OH)_2$ will dissolve in 500 mL of a 0.050-*M* $PbCl_2$ solution (K_{sp} = 1.2 10^{-15})?

56.

Use the simulation from the earlier Link to Learning to complete the following exercise. Using 0.01 g CaF_2, give the K_{sp} values found in a 0.2-*M* solution of each of the salts. Discuss why the values change as you change soluble salts.

57.

How many grams of Milk of Magnesia, $Mg(OH)_2$ (*s*) (58.3 g/mol), would be soluble in 200 mL of water. K_{sp} = 7.1 10^{-12}. Include the ionic reaction and the expression for K_{sp} in your answer. (K_w = 1 10^{-14} = $[H_3O^+][OH^-]$)

58.

Two hypothetical salts, LM_2 and LQ, have the same molar solubility in H_2O. If K_{sp} for LM_2 is 3.20 10^{-5}, what is the K_{sp} value for LQ?

59.

The carbonate ion concentration is gradually increased in a solution containing equal concentrations of the divalent cations of magnesium, calcium, strontium, barium, and manganese. Which of the following carbonates will precipitate first? Which will precipitate last? Explain.

a.

b.

c.

d.

e.

60.

How many grams of $Zn(CN)_2(s)$ (117.44 g/mol) would be soluble in 100 mL of H_2O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $Zn(CN)_2(s)$ is $3.0\ 10^{-16}$.

61.

Even though $Ca(OH)_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of $Ca(OH)_2$?

62.

Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?

63.

Explain why the addition of NH_3 or HNO_3 to a saturated solution of Ag_2CO_3 in contact with solid Ag_2CO_3 increases the solubility of the solid.

64.

Calculate the cadmium ion concentration, $[Cd^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 *M* $Cd(NO_3)_2$ with 0.150 L of 0.100 $NH_3(aq)$.

65.

Explain why addition of NH_3 or HNO_3 to a saturated solution of $Cu(OH)_2$ in contact with solid $Cu(OH)_2$ increases the solubility of the solid.

66.

Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d. For the complex ion the dissociation reaction is:

and

Calculate the value of the formation constant, K_f, for

67.

Using the value of the formation constant for the complex ion calculate the dissociation constant.

68.

Using the dissociation constant, $K_d = 7.8\ 10^{-18}$, calculate the equilibrium concentrations of Cd^{2+} and CN^- in a 0.250-*M* solution of

69.

Using the dissociation constant, $K_d = 3.4\ 10^{-15}$, calculate the equilibrium concentrations of Zn^{2+} and OH^- in a 0.0465-*M* solution of

70.

Using the dissociation constant, $K_d = 2.2\ 10^{-34}$, calculate the equilibrium concentrations of Co^{3+} and NH_3 in a 0.500-*M* solution of

71.

Using the dissociation constant, $K_d = 1\ 10^{-44}$, calculate the equilibrium concentrations of Fe^{3+} and CN^- in a 0.333 M solution of

72.

Calculate the mass of potassium cyanide ion that must be added to 100 mL of solution to dissolve $2.0\ 10^{-2}$ mol of silver cyanide, AgCN.

73.

Calculate the minimum concentration of ammonia needed in 1.0 L of solution to dissolve 3.0 10^{-3} mol of silver bromide.

74.

A roll of 35-mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass of $Na_2S_2O_3 \cdot 5H_2O$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as (K_f = 4.7 10^{13})?

75.

We have seen an introductory definition of an acid: An acid is a compound that reacts with water and increases the amount of hydronium ion present. In the chapter on acids and bases, we saw two more definitions of acids: a compound that donates a proton (a hydrogen ion, H^+) to another compound is called a Brønsted-Lowry acid, and a Lewis acid is any species that can accept a pair of electrons. Explain why the introductory definition is a macroscopic definition, while the Brønsted-Lowry definition and the Lewis definition are microscopic definitions.

76.

Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

a.
b.
c.
d. (use Al-Cl single bonds)
e.

77.

Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

a.
b.
c.
d.
e.

78.

Using Lewis structures, write balanced equations for the following reactions:

a.
b.
c.
d.

79.

Calculate in a solution prepared by adding 0.0200 mol of NaCl to 0.250 L of a 0.100-*M* $HgCl_2$ solution.

80.

In a titration of cyanide ion, 28.72 mL of 0.0100 *M* $AgNO_3$ is added before precipitation begins. [The reaction of Ag^+ with CN^- goes to completion, producing the complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of How many grams of NaCN were in the original sample?

81.

What are the concentrations of Ag^+, CN^-, and in a saturated solution of AgCN?

82.

In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides

that are Lewis acids and accept F^- ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3.

83.

The simplest amino acid is glycine, $H_2NCH_2CO_2H$. The common feature of amino acids is that they contain the functional groups: an amine group, $–NH_2$, and a carboxylic acid group, $–CO_2H$. An amino acid can function as either an acid or a base. For glycine, the acid strength of the carboxyl group is about the same as that of acetic acid, CH_3CO_2H, and the base strength of the amino group is slightly greater than that of ammonia, NH_3.

a. Write the Lewis structures of the ions that form when glycine is dissolved in 1 *M* HCl and in 1 *M* KOH.
b. Write the Lewis structure of glycine when this amino acid is dissolved in water. (Hint: Consider the relative base strengths of the $–NH_2$ and groups.)

84.

Boric acid, H_3BO_3, is not a Brønsted-Lowry acid but a Lewis acid.

a. Write an equation for its reaction with water.
b. Predict the shape of the anion thus formed.
c. What is the hybridization on the boron consistent with the shape you have predicted?

85.

A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?

86.

Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$.

87.

Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of

88.

Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3.

89.

Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^-.

90.

Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 *M* CN^-.

91.

Calculate the Co^{2+} equilibrium concentration when 0.010 mole of $[Co(NH_3)_6](NO_3)_2$ is added to a solution with 0.25 *M* NH_3. Assume the volume is 1.00 L.

92.

Calculate the molar solubility of $Sn(OH)_2$ in a buffer solution containing equal concentrations of NH_3 and

93.

Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 *M* NH_3 and 0.400 *M*

94.

What is the molar solubility of CaF_2 in a 0.100-*M* solution of HF? K_a for HF = $6.4\ 10^{-4}$.

95.

What is the molar solubility of $BaSO_4$ in a 0.250-*M* solution of $NaHSO_4$? K_a for = $1.2\ 10^{-2}$.

96.

What is the molar solubility of $Tl(OH)_3$ in a 0.10-*M* solution of NH_3?

97.

What is the molar solubility of $Pb(OH)_2$ in a 0.138-*M* solution of CH_3NH_2?

98.

A solution of 0.075 *M* $CoBr_2$ is saturated with H_2S ($[H_2S] = 0.10$ *M*). What is the minimum pH at which CoS begins to precipitate?

99.

A 0.125-*M* solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S] = 0.10$ *M*). At what pH does MnS begin to precipitate?

100.

Both AgCl and AgI dissolve in NH_3.

a. What mass of AgI dissolves in 1.0 L of 1.0 *M* NH_3?
b. What mass of AgCl dissolves in 1.0 L of 1.0 *M* NH_3?

101.

The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Solve the following problem:

In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is $1.21\ 10^{-3}$ *M*. The equilibrium is represented by the preceding equation.

a. Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.
b. Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
c. Predict whether a precipitate of MgF_2 will form when 100.0 mL of a $3.00\ 10^{-3}$-*M* solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a $2.00\ 10^{-3}$-*M* solution of NaF at 18 °C. Show the calculations to support your prediction.
d. At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is $1.17\ 10^{-3}$ *M*. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

102.

Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: CuCl, $CaCO_3$, MnS, $PbBr_2$, CaF_2? Explain your answer.

103.

Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_2$, ZnS, PbI_2? Explain your answer.

104.

What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ and water at equilibrium?

a. $MgCl_2$
b. KOH
c. $HClO_4$
d. $NaNO_3$
e. $Mg(OH)_2$

105.

What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?

a. $CaCl_2$
b. HCl
c. $KClO_4$

d. NaOH

e. $CaHPO_4$

106.

Identify all chemical species present in an aqueous solution of $Ca_3(PO_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the ion is a weak base.)

This page titled 15.8: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **15.7: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

CHAPTER OVERVIEW

16: Thermochemistry

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

16.1: Introduction
16.2: Energy Basics
16.3: Calorimetry
16.4: Enthalpy
16.5: Key Terms
16.6: Key Equations
16.7: Summary
16.8: Exercises

This page titled 16: Thermochemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

16.1: Introduction

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



Figure **16.1.1**: Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes)

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

Footnotes

- 1US Energy Information Administration, *Primary Energy Consumption by Source and Sector, 2012*, http://www.eia.gov/totalenergy/data/...012_energy.pdf. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

This page titled 16.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **5.0: Introduction** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

16.2: Energy Basics

Learning Objectives

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

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

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure **16.2.1**). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a) (b) (c)

Figure **16.2.1**: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner)

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

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

Energy

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

the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure **16.2.2**). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **16.2.2**: (a) Water at a higher elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons)

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

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

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

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower average KE, and we say that the object is "cold" (Figure **16.2.3**). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

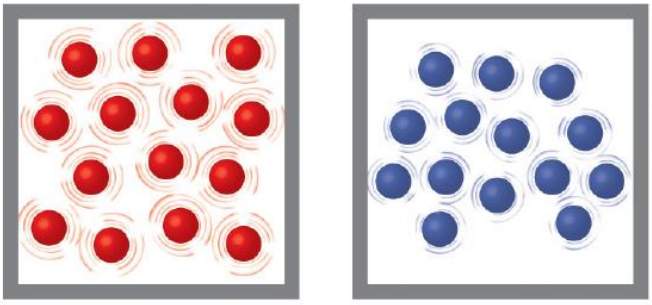


Figure **16.2.3**: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Link to Learning

Click on this interactive simulation to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure **16.2.4**. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

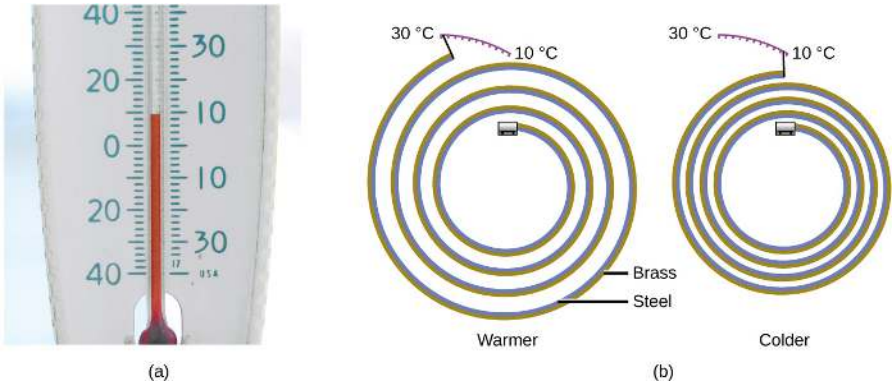


Figure **16.2.4**: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr)

Link to Learning

The following demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure **16.2.5**).

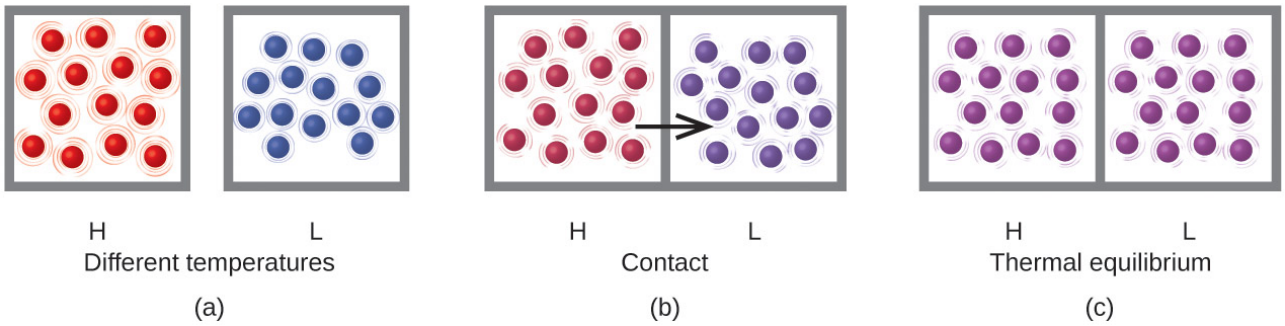


Figure **16.2.5**: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature and their molecules have the same average kinetic energy.

Link to Learning

Click on the PhET simulation to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure **16.2.6**). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure **16.2.6**: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure **16.2.7**).



Figure **16.2.7**: Because of its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Water has a relatively high specific heat (about 4.2 J/g °C for the liquid and 2.09 J/g °C for the solid); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this

variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table **16.2.1**.

Table **16.2.1**: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (*state*)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712

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

$$\begin{aligned} q &= (\text{ specific heat }) \times (\text{ mass of substance }) \times (\text{ temperature change }) \\ &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned} \tag{16.2.1}$$

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

✔ Example 16.2.1: Measuring Heat

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

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 8.0×10^2 g)

- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 8.0×10^2 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 16.2.1:

$$\begin{aligned} q &= c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= \left(4.184 J/\frac{g}{\circ}°C\right) \times (8.0 \times 10^2 g) \times (85 - 21)°C \\ &= (4.184 J/g°C) \times (8.0 \times 10^2 g) \times (64)°C \\ &= 210,000 J \left(= 2.1 \times 10^2 kJ\right) \end{aligned} \tag{16.2.2}$$

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

? Exercise 16.2.1

How much heat, in joules, must be added to a 502 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

Answer

$5.07\ 10^4$ J

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

✓ Example 16.2.2: Determining Other Quantities

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

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship in Equation 16.2.1:

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

Substituting the known values:

$$6640 J = c \times (348 g) \times (43.6 - 22.4)°C$$

Solving:

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

Comparing this value with the values in Table 16.2.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 16.2.2

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

Answer

c = 0.451 J/g °C; the metal is likely to be iron

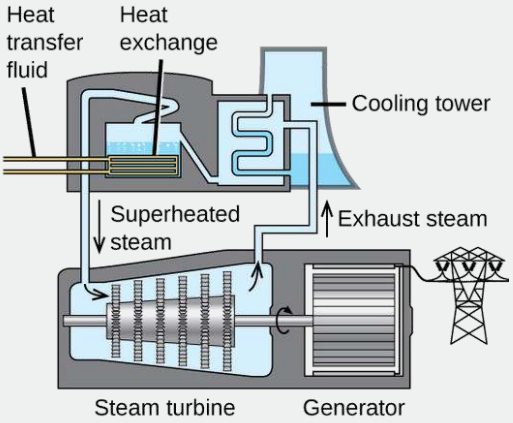
Chemistry in Everyday Life: Solar Thermal Energy Power Plants

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

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure **16.2.8**). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.



(a)



(b)

Figure **16.2.8**: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure **16.2.9**). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a)



(b)

Figure **16.2.9**: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

This page titled 16.2: Energy Basics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **5.1: Energy Basics** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

16.3: Calorimetry

Learning Objectives

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

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

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (all other matter, including components of the measurement apparatus, that serve to either provide heat to the system or absorb heat from the system).

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure **16.3.1**). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

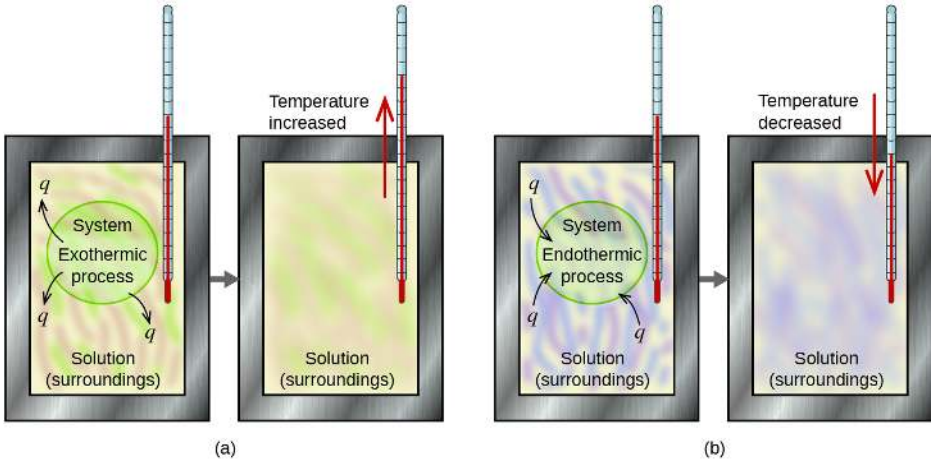


Figure **16.3.1**: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Calorimetry measurements are important in understanding the heat transferred in reactions involving everything from microscopic proteins to massive machines. During her time at the National Bureau of Standards, research chemist Reatha Clark King performed calorimetric experiments to understand the precise heats of various flourine compounds. Her work was important to NASA in their quest for better rocket fuels.

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment, which effectively limits the “surroundings” to the nonsystem components with the calorimeter (and the calorimeter itself). This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure **16.3.2**). These easy-to-use “coffee cup” calorimeters allow more heat exchange with the outside environment, and therefore produce less accurate energy values.

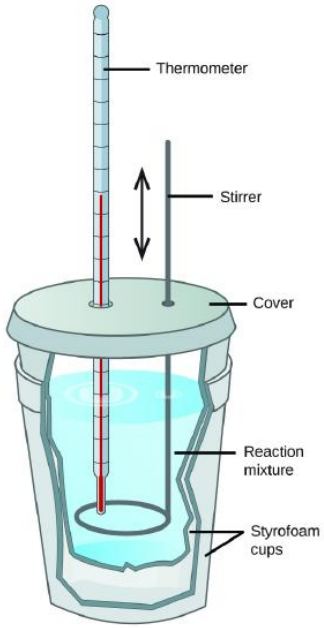


Figure **16.3.2**: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure **16.3.3**).

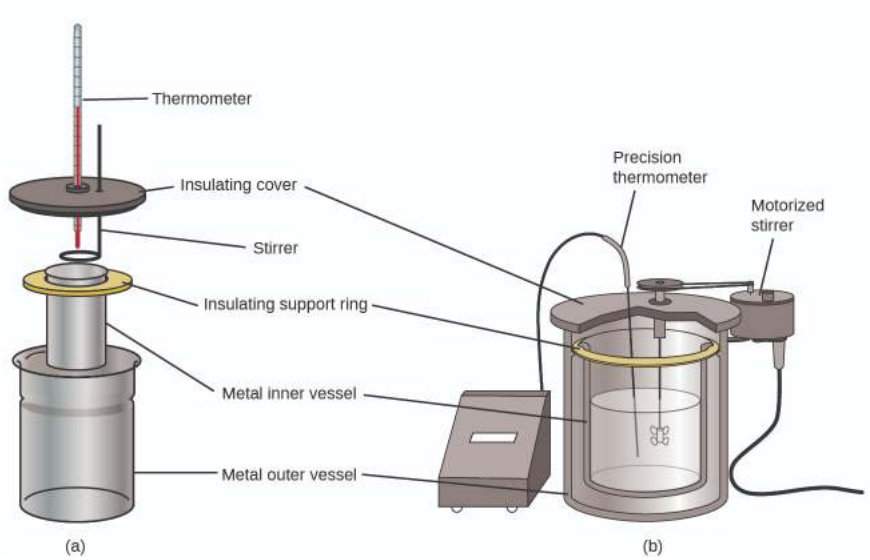


Figure **16.3.3**: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before discussing the calorimetry of chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure **16.3.4**). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either its external environment. Under these ideal circumstances, the net heat change is zero:

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

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

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

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

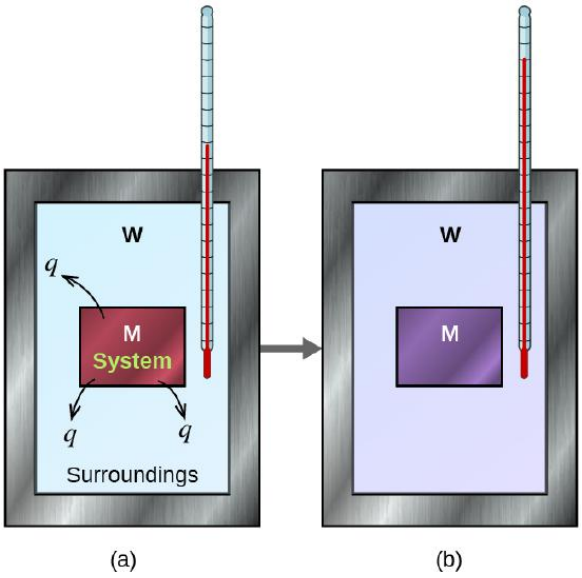


Figure **16.3.4**: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 16.3.1: Heat Transfer between Substances at Different Temperatures

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 was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table 5.1), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

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

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

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

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

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

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

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

$$(0.449 J/g^{\circ}C)\,(360.0 g)\,(42.7^{\circ}C - T_{i,\text{ rebar}}) = -(4.184 J/g^{\circ}C)\,(425 g)\,(42.7^{\circ}C - 24.0^{\circ}C)$$

$$T_{i,\text{ rebar}} = \frac{(4.184 J/g^\circ C)\,(425 g)\,(42.7^\circ C - 24.0^\circ C)}{(0.449 J/g^\circ C)\,(360.0 g)} + 42.7^\circ C$$

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

Exercise 16.3.1A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

Exercise 16.3.1B

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

Answer

The final temperature (reached by both copper and water) is 38.7 °C.

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

Example 16.3.2: Identifying a Metal by Measuring Specific Heat

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

Solution

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

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

In expanded form, this is:

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

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

$$(c_{\text{metal}})\,(59.7 g)\,(28.5^\circ C - 100.0^\circ C) = -(4.18 J/g^\circ C)\,(60.0 g)\,(28.5^\circ C - 22.0^\circ C)$$

Solving this:

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

Comparing this with values in Table 5.1, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 16.3.2

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and

the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

c_{metal}= 0.13 J/g °C

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the outside environment. Because energy is neither created nor destroyed during a chemical reaction, the heat produced or consumed in the reaction (the "system"), \(q_{\text{reaction}}\), plus the heat absorbed or lost by the solution (the "surroundings"), $q_{solution}$, must add up to zero:

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

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

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

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

Example 16.3.3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 1.00 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

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. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

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

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

(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:

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

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0 10^2 g (two significant figures). The specific heat of water is approximately 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{solution} = (4.184 J/g°C)\,(1.0 \times 10^2 g)\,(28.9°C - 22.0°C) = 2.9 \times 10^3 J$$

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

$$q_{reaction} = -q_{solution} = -2.9 \times 10^3 J$$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat.

Exercise 16.3.3

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

Answer

1.34 1.3 kJ; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Chemistry in Everyday Life: Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 16.3.5). A common reusable hand warmer contains a supersaturated solution of $\mathbf{NaC_2H_3O_2}$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $\mathbf{NaC_2H_3O_2}$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process

$$\mathbf{NaC_2H_3O_2\,(aq) \longrightarrow NaC_2H_3O_2\,(s)}$$

is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $\mathbf{NaC_2H_3O_2}$ redissolves and can be reused.



Figure 16.3.5: Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$\mathbf{2\,Fe\,(s) + \tfrac{3}{2}\,O_2\,(g) \longrightarrow Fe_2O_3\,(s)}$$

Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

Link to Learning

This link shows the precipitation reaction that occurs when the disk in a chemical hand warmer is flexed.

Example 16.3.4: Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an "instant ice pack" (Figure 16.3.6). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

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



Figure 16.3.6: An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

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

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

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

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

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

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

Exercise 16.3.4

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

Answer

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water

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

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term “bomb” comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the “bomb”) that contains the reactants and is itself submerged in water (Figure **16.3.7**). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is absorbed by the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known *q*, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.

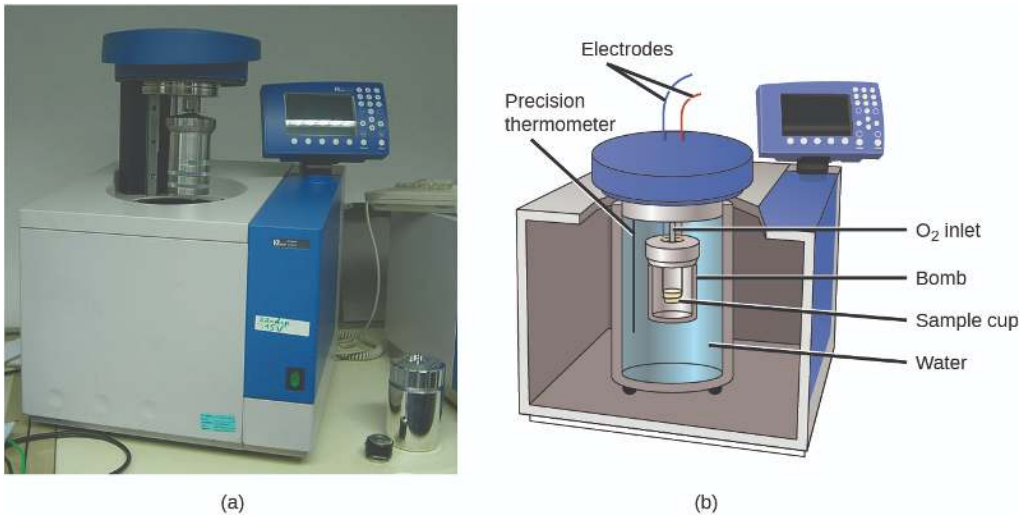


Figure **16.3.7**: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight “bomb,” which is submerged in water and surrounded by insulating materials. (credit a: modification of work by “Harbor1”/Wikimedia commons)

Link to Learning

Click on this link to view how a bomb calorimeter is prepared for action. This site shows calorimetric calculations using sample data.

Example 16.3.5: Bomb Calorimetry

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

Solution

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

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

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

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

Exercise 16.3.5

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

Answer

q_{rx} = –39.0 kJ (the reaction produced 39.0 kJ of heat)

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[2] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes.

For example Carla Prado's team at University of Alberta undertook whole-body calorimetry to understand the energy expenditures of women who had recently given birth. Studies like this help develop better recommendations and regimens for nutrition, exercise, and general wellbeing during this period of significant physiological change. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Chemistry in Everyday Life: Measuring Nutritional Calories

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

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure 16.3.8).

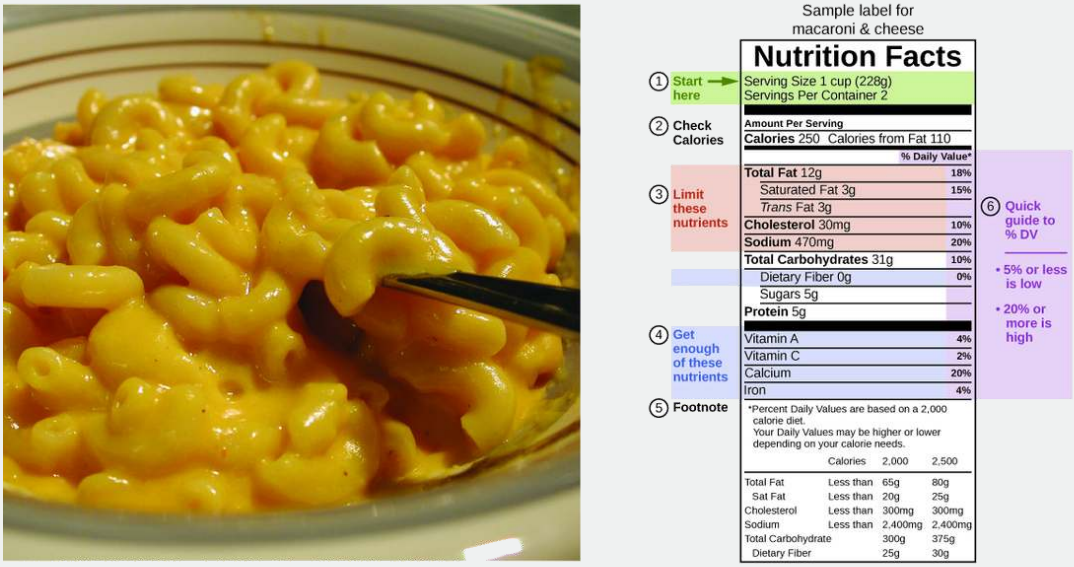


Figure **16.3.8**: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

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

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

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

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

Link to Learning

Click on this link to access the US Department of Agriculture (USDA) National Nutrient Database, containing nutritional information on over 8000 foods.

Footnotes

- 2Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, http://link.springer.com/article/10....517-006-0086-5.

This page titled 16.3: Calorimetry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **5.2: Calorimetry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

16.4: Enthalpy

Learning Objectives

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

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

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

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

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

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

$$\Delta U = q + w$$

as shown in Figure **16.4.1**. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

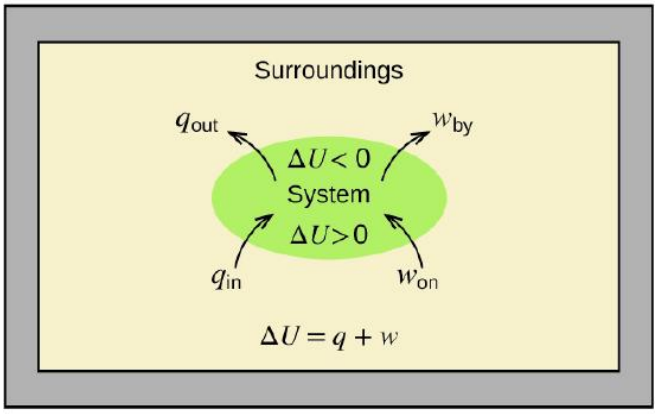


Figure **16.4.1**: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

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

Link to Learning

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

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is an example of a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure **16.4.2**). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

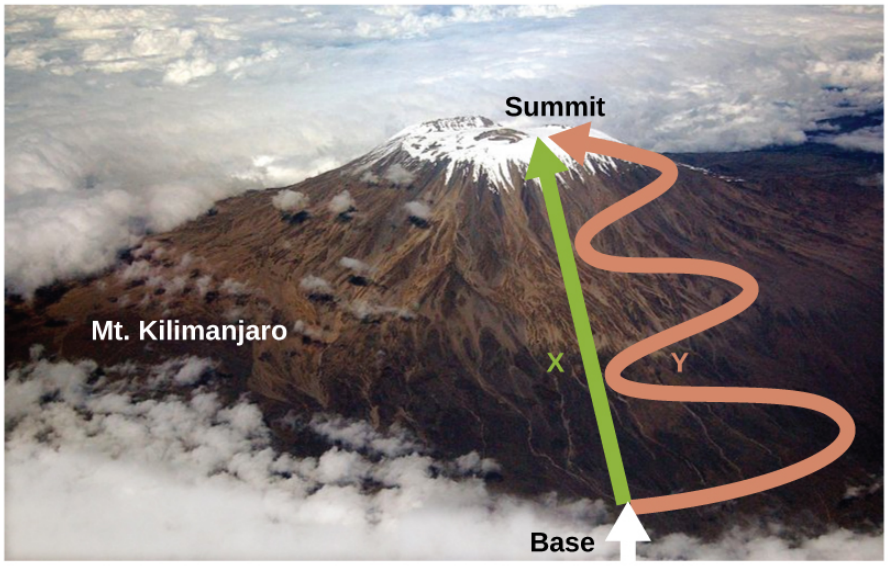


Figure **16.4.2**: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

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

$$H = U + PV$$

Enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

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

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

$$P\Delta V = -w$$

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

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

where q_p is the **heat of reaction** under conditions of constant pressure.

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

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents the pressure from remaining constant (it may increase or decrease if the reaction yields increased or decreased amounts of gaseous species). Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat changes for chemical reactions.

The following conventions apply when using ΔH:

- A negative value of an enthalpy change, $\Delta H < 0$, indicates an exothermic reaction; a positive value, $\Delta H > 0$, indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).
- Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

  $$\mathrm{H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(l)} \quad \Delta H = -286kJ$$

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

  - two-fold increase in amounts

    $$\mathrm{2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)} \quad \Delta H = 2 \times (-286kJ) = -572kJ$$

  - two-fold decrease in amounts

    $$\mathrm{\tfrac{1}{2}\,H_2(g) + \tfrac{1}{4}\,O_2(g) \longrightarrow \tfrac{1}{2}\,H_2O(l)} \quad \Delta H = \frac{1}{2} \times (-286kJ) = -143kJ$$

- The enthalpy change of a reaction depends on the physical states of the reactants and products, so these must be shown. For example, when 1 mole of hydrogen gas and mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

  $$\mathrm{H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(g)} \quad \Delta H = -242kJ$$

Example 16.4.1: Writing Thermochemical Equations

When 0.0500 mol of HCl(aq) reacts with 0.0500 mol of NaOH(aq) to form 0.0500 mol of NaCl(aq), 2.9 kJ of heat are produced. Write a balanced thermochemical equation for the reaction of one mole of HCl.

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. The reactants are provided in stoichiometric amounts (same molar ratio as in the balanced equation), and so the amount of acid may be used to calculate a molar enthalpy change. Since ΔH is an extensive property, it is proportional to the amount of acid neutralized:

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

The thermochemical equation is then

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

? Exercise 16.4.1

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

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

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction.

✓ Example 16.4.2: Writing Thermochemical Equations

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Write a thermochemical equation for the reaction of one mole of sucrose:

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

Solution

Unlike the previous example exercise, this one does not involve the reaction of stoichiometric amounts of reactants, and so the *limiting reactant* must be identified (it limits the yield of the reaction and the amount of thermal energy produced or consumed).

The provided amounts of the two reactants are

$$(2.67\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{342.3\,\mathrm{g}}\right) = 0.00780\,\mathrm{mol\,C_{12}H_{22}O_{11}}$$

$$(7.19\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{122.5\,\mathrm{g}}\right) = 0.0587\,\mathrm{mol\,KClO}$$

The provided molar ratio of perchlorate-to-sucrose is then

$$\frac{0.0587\,\mathrm{mol\ KClO_3}}{0.00780\,\mathrm{mol\,C_{12}H_{22}O_{11}}} = 7.52$$

The balanced equation indicates 8 mol $KClO_3$ are required for reaction with 1 mol $C_{12}H_{22}O_{11}$. Since the provided amount of $KClO_3$ is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

$$\Delta H = \frac{-43.7\,\mathrm{kJ}}{0.0587\,\mathrm{molKClO_3}} = \frac{744\,\mathrm{kJ}}{\mathrm{mol\,KClO_3}}$$

Because the equation, as written, represents the reaction of 8 mol $KClO_3$, the enthalpy change is

$$\left(\frac{744\,\mathrm{kJ}}{1\ \cancel{\mathrm{mol\,KClO_3}}}\right)\left(8\ \cancel{\mathrm{mol\,KClO_3}}\right) = 5960\,\mathrm{kJ}$$

The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl \quad \Delta H = -5960\,kJ$$

? Exercise 16.4.1

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

Answer

ΔH = −338 kJ

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

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Standard Enthalpy of Combustion

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

$$C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2 + 3\,H_2O(l) \quad \Delta H^\circ = -1366.8\,kJ$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 16.4.1. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table 16.4.1: Standard Molar Enthalpies of Combustion

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

Example 16.4.3: Using Enthalpy of Combustion

As Figure **16.4.3**: suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



Figure **16.4.3**: The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table **16.4.1** gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

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

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

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

$$1.00\,\text{L}\,C_8H_{18} \longrightarrow 1.00 \times 10^3\,\text{mL}C_8H_{18}$$
$$1.00 \times 10^3\,\text{mL}\,C_8H_{18} \longrightarrow 692\,\text{g}\,C_8H_{18}$$
$$692\,\text{g}\,C_8H_{18} \longrightarrow 6.07\,\text{mol}\,C_8H_{18}$$
$$6.07\,\text{mol}\,C_8H_{18} \longrightarrow -3.31 \times 10^4 kJ$$

? Exercise 16.4.3

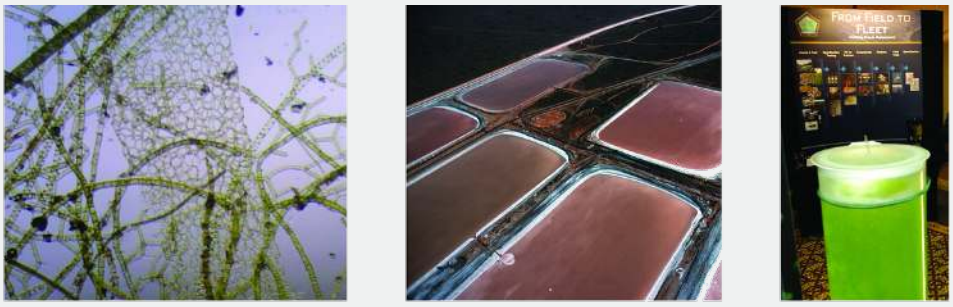
How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25 10^3 kJ

Chemistry in Everyday Life: Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 5.22). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.



(a) (b) (c)

Figure 5.22 (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon.[3] The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure **16.4.4**).

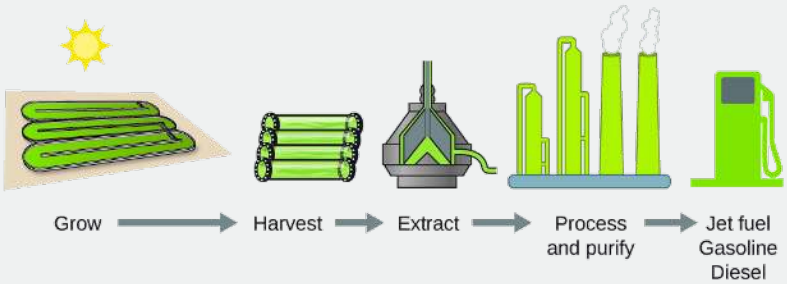


Figure **16.4.4**: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Link to Learning

Click here to learn more about the process of creating algae biofuel.

Standard Enthalpy of Formation

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

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

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_f^\circ = \Delta H^\circ = -393.5\,kJ}$$

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

$$\mathrm{\tfrac{1}{2}\,N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta H_f^\circ = \Delta H^\circ = +33.2\,kJ}$$

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

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

Example 16.4.4: Evaluating an Enthalpy of Formation

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

$$\mathrm{3\,O_2(g) \longrightarrow 2\,O_3(g) \quad \Delta H^\circ = +286\,kJ}$$

Solution

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

$$\mathrm{\tfrac{3}{2}\,O_2(g) \longrightarrow O_3(g)}$$

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

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

Therefore,

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

Exercise 16.4.4

Hydrogen gas, $\mathrm{H_2}$, reacts explosively with gaseous chlorine, $\mathrm{Cl_2}$, to form hydrogen chloride, $\mathrm{HCl(g)}$. What is the enthalpy change for the reaction of 1 mole of $\mathrm{H_2(g)}$ with 1 mole of $\mathrm{Cl_2(g)}$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $\mathrm{HCl(g)}$ is −92.3 kJ/mol.

Answer

For the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H^\circ = -184.6\,kJ$$

Example 16.4.5: Writing Reaction Equations for

Write the heat of formation reaction equations for:

a. $C_2H_5OH(l)$
b. $Ca_3(PO_4)_2(s)$

Solution

Remembering that reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $$2\,C(s, \text{graphite}) + 3\,H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_5OH(l)$$

b. $$3\,Ca(s) + \tfrac{1}{2}\,P_4(s) + 4\,O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 16.4.5

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_5(l)$
b. $Na_2CO_3(s)$

Answer

a. $$4\,C(s, \text{graphite}) + 5\,H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_5OC_2H_5(l)$$

b. $$2\,Na(s) + C(s, \text{graphite}) + \tfrac{3}{2}\,O_2(g) \longrightarrow Na_2CO_3(s)$$

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess's law, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps*. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ = -394kJ$$

In the two-step process, first carbon monoxide is formed:

$$C(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO(g) \quad \Delta H^\circ = -111kJ$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ = -283kJ$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{array}{ll} \text{step 1} & \mathrm{C(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO(g)} \\ \text{step 2} & \mathrm{CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)} \\ \hline \text{sum} & \mathrm{C(s) + \cancel{CO(g)} + O_2(g) \longrightarrow \cancel{CO(g)} + CO_2(g)} \end{array}$$

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.

$$\begin{array}{lll} \text{step 1} & \mathrm{C(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow \cancel{CO(g)}} & \Delta H^\circ = -111\,\mathrm{kJ} \\ \text{step 2} & \mathrm{\cancel{CO(g)} + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)} & \Delta H^\circ = -283\,\mathrm{kJ} \\ \hline \text{sum} & \mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)} & \Delta H^\circ = -394\,\mathrm{kJ} \end{array}$$

The result is shown in Figure **16.4.5**. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

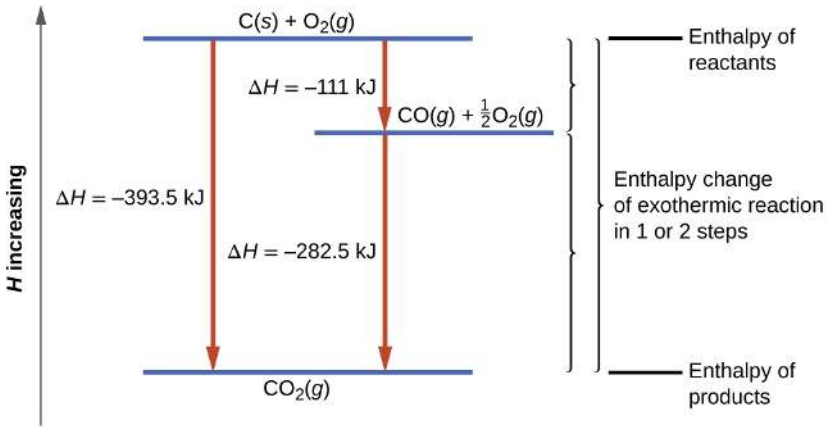


Figure **16.4.5**: The formation of $\mathrm{CO_2(g)}$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

   $$\mathrm{\tfrac{1}{2}\,N_2(g) + O_2(g) \longrightarrow NO_2(g)} \quad \Delta H = +33.2\,\mathrm{kJ}$$

   When 2 moles of $\mathrm{NO_2}$ (twice as much) are formed, the ΔH will be twice as large:

   $$\mathrm{N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)} \quad \Delta H = +66.4\,\mathrm{kJ}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to $\Delta H$for the reaction in the reverse direction. For example, given that:

   $$\mathrm{H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g)} \quad \Delta H = -184.6\,\mathrm{kJ}$$

   Then, for the "reverse" reaction, the enthalpy change is also "reversed":

Example 16.4.6: Stepwise Calculation of Heat of Formation Using Hess's Law

Determine the enthalpy of formation, of $\mathrm{FeCl_3(s)}$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s)} \quad \Delta H^\circ = -341.8\,\mathrm{kJ}$$

$$\mathrm{FeCl_2(s) + \tfrac{1}{2}\,Cl_2(g) \longrightarrow FeCl_3(s)} \quad \Delta H^\circ = -57.7\,\mathrm{kJ}$$

Solution

We are trying to find the standard enthalpy of formation of $\mathrm{FeCl_3(s)}$, which is equal to ΔH° for the reaction:

$$\mathrm{Fe(s) + \tfrac{3}{2}\,Cl_2(g) \longrightarrow FeCl_3(s)} \quad \Delta H_f^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their ΔH values:

step 1	$\mathrm{Fe(s) + Cl_2(g) \longrightarrow \cancel{FeCl2(s)}}$	$\Delta H^\circ = -341.8\,\mathrm{kJ}$
step 2	$\mathrm{\cancel{FeCl2(s)} + \tfrac{1}{2}\,Cl_2(g) \longrightarrow FeCl_3(s)}$	$\Delta H^\circ = -57.7\,\mathrm{kJ}$
sum	$\mathrm{Fe(s) + \tfrac{3}{2}\,Cl_2(g) \longrightarrow FeCl_3(s)}$	$\Delta H^\circ = -399.5\,\mathrm{kJ}$

The enthalpy of formation, ΔH_f° of $\mathrm{FeCl_3(s)}$ is −399.5 kJ/mol.

Exercise 16.4.6

Calculate ΔH for the process:

$$\mathrm{N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)}$$

from the following information:

$$\mathrm{N_2(g) + O_2(g) \longrightarrow 2\,NO(g)} \quad \Delta H = 180.5\,\mathrm{kJ}$$

$$\mathrm{NO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow NO_2(g)} \quad \Delta H = -57.06\,\mathrm{kJ}$$

Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of ΔH) if they are difficult to determine experimentally.

Example 16.4.7: A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

i. $$\mathrm{ClF(g) + F_2(g) \longrightarrow ClF_3(g)} \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction (i):

ii. $$\mathrm{2\,OF_2(g) \longrightarrow O_2(g) + 2\,F_2(g)} \quad \Delta H^\circ_{(ii)} = -49.4\,\mathrm{kJ}$$

iii. $$\mathrm{2\,ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g)} \quad \Delta H^\circ_{(iii)} = +214.0\,\mathrm{kJ}$$

iv. $$\mathrm{ClF_3(g) + O_2(g) \longrightarrow \tfrac{1}{2}\,Cl_2O(g) + \tfrac{3}{2}\,OF_2(g)} \quad \Delta H^\circ_{(in)} = +236.2\,\mathrm{kJ}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that ClF(g) is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$ which means that the ΔH^o change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \tfrac{1}{2}\,\mathrm{Cl_2O\,(g)} + \tfrac{1}{2}\,\mathrm{OF_2\,(g)} \quad \Delta H^\circ = \frac{1}{2}(214.0) = +107.0\,\mathrm{kJ}$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction *(ii)*, which means that the ΔH^o changes sign and is halved:

$$\tfrac{1}{2}\,\mathrm{O_2\,(g)} + \mathrm{F_2\,(g)} \longrightarrow \mathrm{OF_2\,(g)} \quad \Delta H^\circ = +24.7\,\mathrm{kJ}$$

To get $\mathrm{ClF_3}$ as a product, reverse (iv), changing the sign of ΔH^o:

$$\tfrac{1}{2}\,\mathrm{Cl_2O\,(g)} + \tfrac{3}{2}\,\mathrm{OF_2\,(g)} \longrightarrow \mathrm{ClF_3\,(g)} + \mathrm{O_2\,(g)} \quad \Delta H^\circ = -236.2kJ$$

Now check to make sure that these reactions add up to the reaction we want:

step 1	$\mathrm{ClF\,(g)} + \cancel{1/2O2(g)} \longrightarrow \cancel{1/2Cl2O(g)} + \cancel{1/2OF2(g)}$	$\Delta H^\circ = +107.0\,\mathrm{kJ}$
step 2	$\cancel{1/2O2(g)} + \mathrm{F_2\,(g)} \longrightarrow \cancel{OF2(g)}$	$\Delta H^\circ = +24.7\,\mathrm{kJ}$
step 3	$\cancel{1/2Cl2O(g)} + \cancel{3/2OF2(g)} \longrightarrow \mathrm{ClF_3\,(g)} + \cancel{O2(g)}$	$\Delta H^\circ = -236.2\,\mathrm{kJ}$
sum	$\mathrm{ClF\,(g)} + \mathrm{F_2\,(g)} \longrightarrow \mathrm{ClF_3\,(g)}$	$\Delta H^\circ = -104.5\,\mathrm{kJ}$

Reactants $\frac{1}{2}\,\mathrm{O_2}$ and $\frac{1}{2}\,\mathrm{O_2}$ cancel out the product $\mathrm{O_2}$; the $\frac{1}{2}\,\mathrm{Cl_2O}$ product cancels $\frac{1}{2}\,\mathrm{Cl_2O}$ reactant and $\frac{3}{2}\,\mathrm{Cl_2O}$ reactant is cancelled by products $\frac{1}{2}\,\mathrm{OF_2}$ and $\mathrm{OF_2}$. This leaves only reactants $\mathrm{ClF\,(g)}$ and $\mathrm{F_2\,(g)}$ and product $\mathrm{ClF_3\,(g)}$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH^o values will give the desired ΔH^o:

$$\Delta H^\circ = (+107.0kJ) + (24.7kJ) + (-236.2kJ) = -104.5\,\mathrm{kJ}$$

? Exercise 16.4.7

Aluminum chloride can be formed from its elements:

i. $$\mathrm{2\,Al\,(s) + 3\,Cl_2\,(g) \longrightarrow 2\,AlCl_3\,(s)} \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction *(i)*:

ii. $$\mathrm{HCl\,(g) \longrightarrow HCl\,(aq)} \quad \Delta H^\circ_{(ii)} = -74.8\,\mathrm{kJ}$$

iii. $$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)} \quad \Delta H^\circ_{(iii)} = -185\,\mathrm{kJ}$$

iv. $$\mathrm{AlCl_3\,(aq) \longrightarrow AlCl_3\,(s)} \quad \Delta H^\circ_{(iv)} = +323\,\mathrm{kJ}$$

v. $$\mathrm{2\,Al\,(s) + 6\,HCl\,(aq) \longrightarrow 2\,AlCl_3\,(aq) + 3\,H_2\,(g)} \quad \Delta H^\circ_{(v)} = -1049\,\mathrm{kJ}$$

Answer

−1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are:

i. decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by
ii. re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products).

The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with ∑ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants })$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 16.4.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,NO_2\,(g) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g) \quad \Delta H^\circ = ?$$

Solution: Using the Equation

Use the special form of Hess's law given previously, and values from Appendix G:

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants }) \\
&= \left[2\ \cancel{\text{mol HNO}_3\,(aq)} \times \frac{-207.4\,\text{kJ}}{1\ \cancel{\text{mol HNO}_3\,(aq)}} + 1\ \cancel{\text{mol NO}\,(g)} \times \frac{+90.2\,\text{kJ}}{1\ \cancel{\text{mol NO}\,(g)}}\right] \\
&\quad - \left[3\ \cancel{\text{mol NO}_2\,(g)} \times \frac{+33.2\,\text{kJ}}{1\ \cancel{\text{mole NO}_2\,(g)}} + 1\ \cancel{\text{mol H}_2\text{O}\,(l)} \times \frac{-285.8\,\text{kJ}}{1\ \cancel{\text{mol H}_2\text{O}\,(l)}}\right] \\
&= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)] \\
&= -323.03 + 186.23 \\
&= -136.80\,\text{kJ}
\end{aligned}$$

Solution: Supporting Why the General Equation is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\,NO_2\,(g)$ and $H2O(l)$ into their constituent elements, and the formation of $2\,HNO_3\,(aq)$ and $1\,NO\,(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH° values for these compounds (from Appendix G), we have:

$$\begin{aligned}
3\,NO_2\,(g) &\longrightarrow \tfrac{3}{2}\,N_2\,(g) + 3\,O_2\,(g) && \Delta H^\circ_1 = -99.6\,\text{kJ} \\
H_2O\,(l) &\longrightarrow H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) && \Delta H^\circ_2 = +285.8\,\text{kJ}\ \left[-1 \times \Delta H^\circ_f\,(H_2O)\right] \\
H_2\,(g) + N_2\,(g) + 3\,O_2\,(g) &\longrightarrow 2\,HNO_3\,(aq) && \Delta H^\circ_3 = -414.8\,\text{kJ}\ \left[2 \times \Delta H^\circ_f\,(HNO_3)\right] \\
\tfrac{1}{2}\,N_2\,(g) + \tfrac{1}{2}\,O_2\,(g) &\longrightarrow NO\,(g) && \Delta H^\circ_4 = +90.2\,\text{kJ}\ \left[1 \times \Delta H^\circ_f(NO)\right]
\end{aligned}$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,NO_2\,(g) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\begin{aligned}
\Delta H^\circ_{rxn} &= \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 \\
&= (-99.6\,\text{kJ}) + (+285.8\,\text{kJ}) + (-414.8\,\text{kJ}) + (+90.2\,\text{kJ}) \\
&= -138.4\,\text{kJ}
\end{aligned}$$

So the standard enthalpy change for this reaction is ΔH° = −138.4 kJ.

Note that this result was obtained by:

a. multiplying the of each product by its stoichiometric coefficient and summing those values,
b. multiplying the of each reactant by its stoichiometric coefficient and summing those values, and then
c. subtracting the result found in (2) from the result found in (1).

This is also the procedure in using the general equation, as shown.

Exercise 16.4.8

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH\,(l)$, when $H_2O\,(l)$ and $CO_2\,(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH\,(l)$, −278 kJ/mol; $H_2O\,(l)$, −286 kJ/mol; and $CO_2\,(g)$, −394 kJ/mol.

Answer

−1368 kJ/mol

Footnotes

- 3For more on algal fuel, see http://www.theguardian.com/environme...n-fuel-problem.

This page titled 16.4: Enthalpy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **5.3: Enthalpy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

16.5: Key Terms

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

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

calorimeter | device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry | process of measuring the amount of heat involved in a chemical or physical process

chemical thermodynamics | area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

endothermic process | chemical reaction or physical change that absorbs heat

energy | capacity to supply heat or do work

enthalpy (*H*) | sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH) | heat released or absorbed by a system under constant pressure during a chemical or physical process

exothermic process | chemical reaction or physical change that releases heat

expansion work (pressure-volume work) | work done as a system expands or contracts against external pressure

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

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)

Hess's law | if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon | compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (*U*) | total of all possible kinds of energy present in a substance or substances

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

kinetic energy | energy of a moving body, in joules, equal to (where m = mass and v = velocity)

nutritional calorie (Calorie) | unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

potential energy | energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (*c*) | intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

standard enthalpy of combustion | heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation | enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state | set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function | 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 | portion of matter undergoing a chemical or physical change being studied

temperature | intensive property of matter that is a quantitative measure of "hotness" and "coldness"

thermal energy | kinetic energy associated with the random motion of atoms and molecules

thermochemistry | study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (*w*) | energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

16.5: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.4: Key Terms** is licensed CC BY 4.0.

16.6: Key Equations

16.6: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.5: Key Equations** is licensed CC BY 4.0.

16.7: Summary

Energy is the capacity to supply heat or do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics).

The thermal energy of matter is due to the kinetic energies of its constituent atoms or molecules. Temperature is an intensive property of matter reflecting hotness or coldness that increases as the average kinetic energy increases. Heat is the transfer of thermal energy between objects at different temperatures. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J).

Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations.

Calorimeters are designed to minimize energy exchange between their contents and the external environment. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or for reactions occurring under standard state conditions at 298 K. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. The standard enthalpy of formation, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar and 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

16.7: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.6: Summary** is licensed CC BY 4.0.

16.8: Exercises

1.

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

2.

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

3.

Explain the difference between heat capacity and specific heat of a substance.

4.

Calculate the heat capacity, in joules and in calories per degree, of the following:

a. 28.4 g of water
b. 1.00 oz of lead

5.

Calculate the heat capacity, in joules and in calories per degree, of the following:

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

6.

How much heat, in joules and in calories, must be added to a 75.0–g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

7.

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

8.

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

9.

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

10.

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

a. What is the specific heat of the substance?
b. If it is one of the substances found in Table 5.1, what is its likely identity?

11.

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

a. What is the specific heat of the substance?
b. If it is one of the substances found in Table 5.1, what is its likely identity?

12.

An aluminum kettle weighs 1.05 kg.

a. What is the heat capacity of the kettle?
b. How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?
c. How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific heat of 4.184 J/g °C)?

13.

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6 10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?

14.

A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.

15.

Would the amount of heat measured for the reaction in Example 5.5 be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

16.

Would the amount of heat absorbed by the dissolution in Example 5.6 appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

17.

Would the amount of heat absorbed by the dissolution in Example 5.6 appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

18.

How many milliliters of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

19.

How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

20.

A 45-g aluminum spoon (specific heat 0.88 J/g °C) at 24 °C is placed in 180 mL (180 g) of coffee at 85 °C and the temperature of the two become equal.

a. What is the final temperature when the two become equal? Assume that coffee has the same specific heat as water.
b. The first time a student solved this problem she got an answer of 88 °C. Explain why this is clearly an incorrect answer.

21.

The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.

22.

A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in Figure 5.12. The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?

23.

If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure 5.12, what is the resulting temperature of the water?

24.

A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter (Figure 5.12). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

25.

Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter (Figure 5.12) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

26.

When 50.0 g of 0.200 M NaCl(*aq*) at 24.1 °C is added to 100.0 g of 0.100 M $AgNO_3(aq)$ at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as AgCl(*s*) forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.

27.

The addition of 3.15 g of $Ba(OH)_2{\cdot}8H_2O$ to a solution of 1.52 g of NH_4SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:

$$Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(aq) \longrightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

28.

The reaction of 50 mL of acid and 50 mL of base described in Example 5.5 increased the temperature of the solution by 6.9 ºC. How much would the temperature have increased if 100 mL of acid and 100 mL of base had been used in the same calorimeter starting at the same temperature of 22.0 ºC? Explain your answer.

29.

If the 3.21 g of NH_4NO_3 in Example 5.6 were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.

30.

When 1.0 g of fructose, $C_6H_{12}O_6(s)$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is *q* for this combustion?

31.

When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?

32.

One method of generating electricity is by burning coal to heat water, which produces steam that drives an electric generator. To determine the rate at which coal is to be fed into the burner in this type of plant, the heat of combustion per ton of coal must be determined using a bomb calorimeter. When 1.00 g of coal is burned in a bomb calorimeter (Figure 5.17), the temperature increases by 1.48 °C. If the heat capacity of the calorimeter is 21.6 kJ/°C, determine the heat produced by combustion of a ton of coal (2.000 10^3 pounds).

33.

The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is
9.1 Calories/g?

34.

A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?

35.

What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g?

36.

A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1 10^3 Calories if the average number of Calories for fat is
9.1 Calories/g?

37.

A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

38.

Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs $4.23, or a liter of isooctane (density, 0.6919 g/mL) that costs $0.45? Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

39.

Explain how the heat measured in Example 5.5 differs from the enthalpy change for the exothermic reaction described by the following equation:

40.

Using the data in the check your learning section of Example 5.5, calculate ΔH in kJ/mol of $AgNO_3(aq)$ for the reaction:

41.

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of NH_4NO_3 under the conditions described in Example 5.6.

42.

Calculate ΔH for the reaction described by the equation. (*Hint*: Use the value for the approximate amount of heat absorbed by the reaction that you calculated in a previous exercise.)

43.

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $CaCl_2$ (refer to Exercise 5.25).

44.

Although the gas used in an oxyacetylene torch (Figure 5.7) is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in Table 5.2. Considering the conditions for which the tabulated data are reported, suggest an explanation.

45.

How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

46.

How much heat is produced by combustion of 125 g of methanol under standard state conditions?

47.

How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

48.

What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

49.

When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

50.

How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?

If both solutions are at the same temperature and the specific heat of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?

51.

A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

52.

Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl_2F_2 (enthalpy of vaporization is 17.4 kJ/mol)?

The vaporization reactions for SO_2 and CCl_2F_2 are and respectively.

53.

Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

54.

Which of the enthalpies of combustion in Table 5.2 the table are also standard enthalpies of formation?

55.

Does the standard enthalpy of formation of $H_2O(g)$ differ from $\Delta H°$ for the reaction

56.

Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red $HgO(s)$ to $Hg(l)$ and $O_2(g)$ under standard conditions?

57.

How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $Mn_3O_4(s)$ at standard state conditions?

58.

How many kilojoules of heat will be released when exactly 1 mole of iron, Fe, is burned to form $Fe_2O_3(s)$ at standard state conditions?

59.

The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

60.

Both graphite and diamond burn.

For the conversion of graphite to diamond:

Which produces more heat, the combustion of graphite or the combustion of diamond?

61.

From the molar heats of formation in Appendix G, determine how much heat is required to evaporate one mole of water:

62.

Which produces more heat?

or

for the phase change

63.

Calculate for the process

from the following information:

64.

Calculate for the process

from the following information:

65.

Calculate ΔH for the process

from the following information:

66.

Calculate for the process

from the following information:

67.

Calculate the standard molar enthalpy of formation of NO(g) from the following data:

68.

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

a.
b.
c.
d.

69.

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

a.
b.
c.
d.

70.

The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.

a.

b.

c.

d.

71.

The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix G, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

72.

Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is −104 kJ/mol.

73.

Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is −126 kJ/mol.

74.

Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?

75.

The white pigment TiO_2 is prepared by the reaction of titanium tetrachloride, $TiCl_4$, with water vapor in the gas phase:

How much heat is evolved in the production of exactly 1 mole of $TiO_2(s)$ under standard state conditions?

76.

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon:

a. Under the conditions of the reaction, methanol forms as a gas. Calculate for this reaction and for the condensation of gaseous methanol to liquid methanol.

(c) Calculate the heat of combustion of 1 mole of liquid methanol to $H_2O(g)$ and $CO_2(g)$.

77.

In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2. Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2:

Calculate the standard enthalpy of the reaction. The of CaC_2 is −15.14 kcal/mol.

78.

From the data in Table 5.2, determine which of the following fuels produces the greatest amount of heat per gram when burned under standard conditions: $CO(g)$, $CH_4(g)$, or $C_2H_2(g)$.

79.

The enthalpy of combustion of hard coal averages −35 kJ/g, that of gasoline, 1.28 10^5 kJ/gal. How many kilograms of hard coal provide the same amount of heat as is available from 1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

80.

Ethanol, C_2H_5OH, is used as a fuel for motor vehicles, particularly in Brazil.

a. Write the balanced equation for the combustion of ethanol to $CO_2(g)$ and $H_2O(g)$, and, using the data in Appendix G, calculate the enthalpy of combustion of 1 mole of ethanol.
b. The density of ethanol is 0.7893 g/mL. Calculate the enthalpy of combustion of exactly 1 L of ethanol.

c. Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n–octane, C_8H_{18} density = 0.7025 g/mL).

81.

Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B_2H_6, produces $B_2O_3(s)$ and $H_2O(g)$], methane [CH_4, produces $CO_2(g)$ and $H_2O(g)$], and hydrazine [N_2H_4, produces $N_2(g)$ and $H_2O(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The

82.

How much heat is produced when 1.25 g of chromium metal reacts with oxygen gas under standard conditions?

83.

Ethylene, C_2H_4, a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst.

Using the data in the table in Appendix G, calculate $\Delta H°$ for the reaction.

84.

The oxidation of the sugar glucose, $C_6H_{12}O_6$, is described by the following equation:

The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.

a. How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?
b. How many Calories can be produced by the metabolism of 1.0 g of glucose?

85.

Propane, C_3H_8, is a hydrocarbon that is commonly used as a fuel.

a. Write a balanced equation for the complete combustion of propane gas.
b. Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: We will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2.)
c. The heat of combustion of propane is −2,219.2 kJ/mol. Calculate the heat of formation, of propane given that of $H_2O(l)$ = −285.8 kJ/mol and of $CO_2(g)$ = −393.5 kJ/mol.
d. Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

86.

During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).

a. (f) How many kilowatt–hours (1 kWh = 3.6 10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.

   (g) Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

This page titled 16.8: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **5.7: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

CHAPTER OVERVIEW

17: Thermodynamics

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

17.1: Introduction
17.2: Spontaneity
17.3: Entropy
17.4: The Second and Third Laws of Thermodynamics
17.5: Free Energy
17.6: Key Terms
17.7: Key Equations
17.8: Summary
17.9: Exercises

This page titled 17: Thermodynamics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

17.1: Introduction

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.



Figure **17.1.1**: Geysers are a dramatic display of thermodynamic principles in nature. Water deep within the underground channels of the geyser is under high pressure and heated to high temperature by magma. When a pocket of water near the surface reaches boiling point and is expelled, the resulting drop in pressure causes larger volumes of water to flash boil, forcefully ejecting steam and water in an impressive eruption. (credit: modification of work by Yellowstone National Park)

17.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **16.0: Introduction** is licensed CC BY 4.0.

17.2: Spontaneity

Learning Objectives

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

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure **17.2.1**).

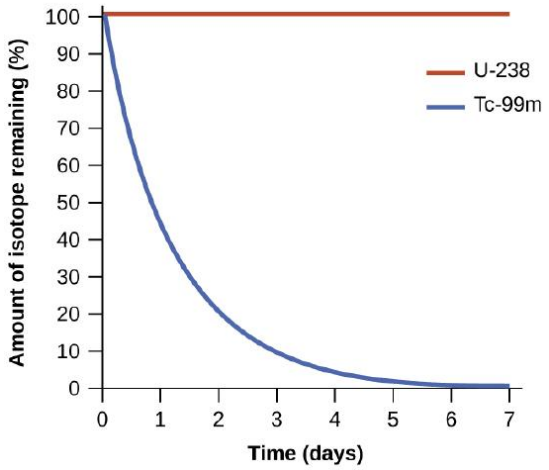


Figure **17.2.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure **17.2.2**).

$$C(s, \text{diamond}) \longrightarrow C(s, \text{graphite})$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a

process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

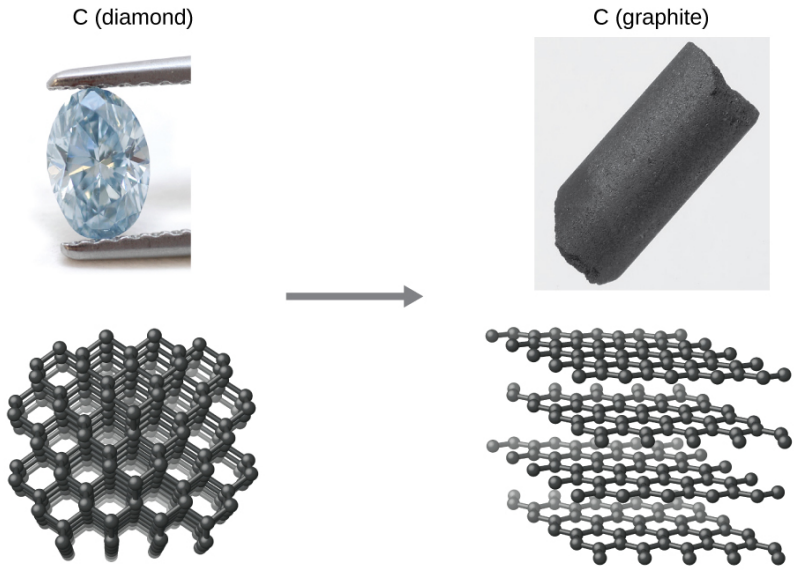


Figure **17.2.2**: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values 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)

Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$) (Figure **17.2.3**). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

\[w=-P \Delta V=0 \quad \quad (P=0 \text { in a vacuum })|]

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

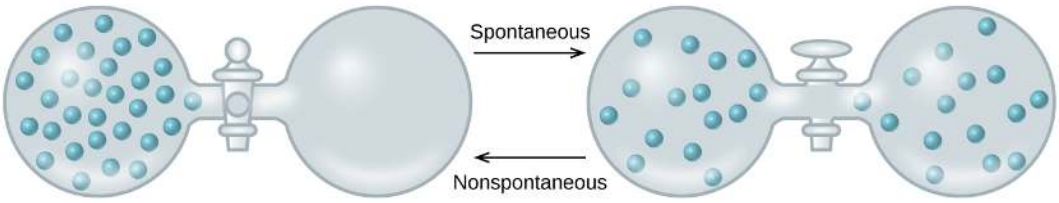


Figure **17.2.3**: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure **17.2.4**). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y).

This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



$T_X > T_Y$ X and Y in contact

Figure **17.2.4**: When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 17.2.1: Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



(a) (b) (c)

Figure **17.2.5**: (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

a. Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.
b. Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.
c. The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Exercise 17.2.1

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer

Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

This page titled 17.2: Spontaneity is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **16.1: Spontaneity** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

17.3: Entropy

Learning Objectives

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

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure **17.3.1**) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot's findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). In thermodynamics, a **reversible process** is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

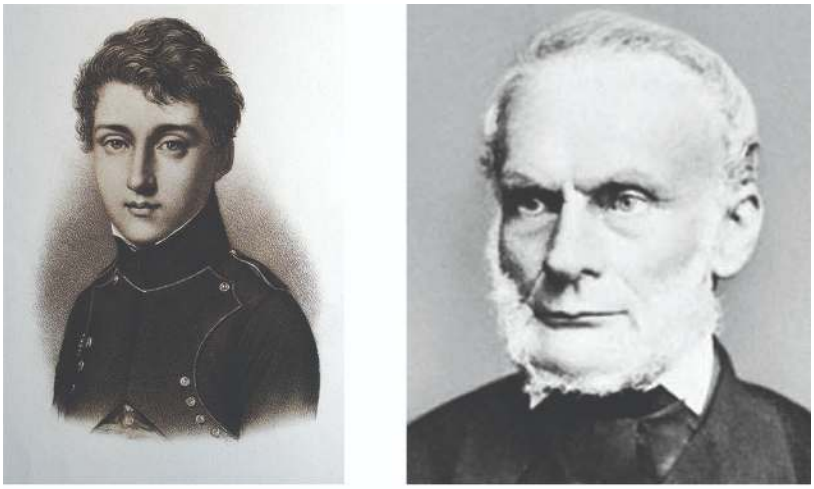


Figure **17.3.1**: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{rev}}{T}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of microstates* (W) possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38 10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure **17.3.2**. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

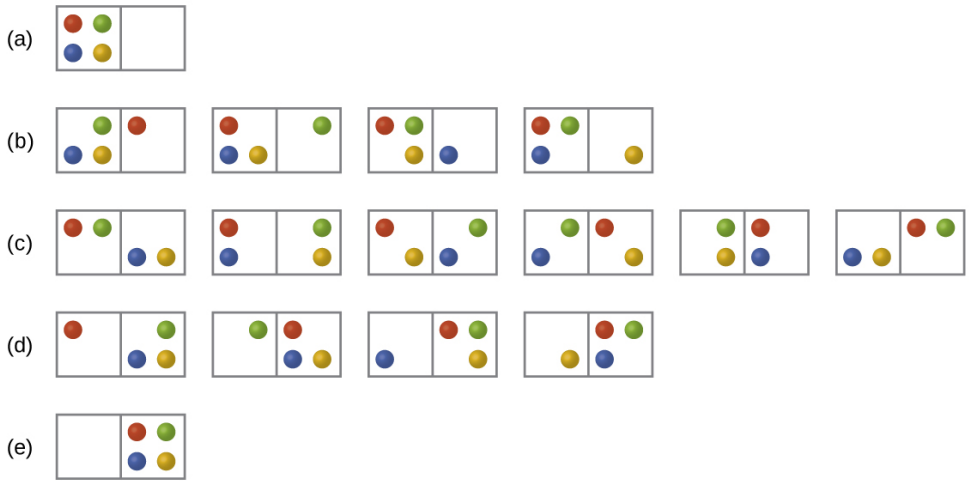


Figure **17.3.2**: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$ or $\frac{3}{8}$ The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of The probability of finding all particles in only one box (either the left box or right box) is then or

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} \text{ or } \frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (Figure 16.4) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of thermal energy (represented as "*") in Figure **17.3.3**. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

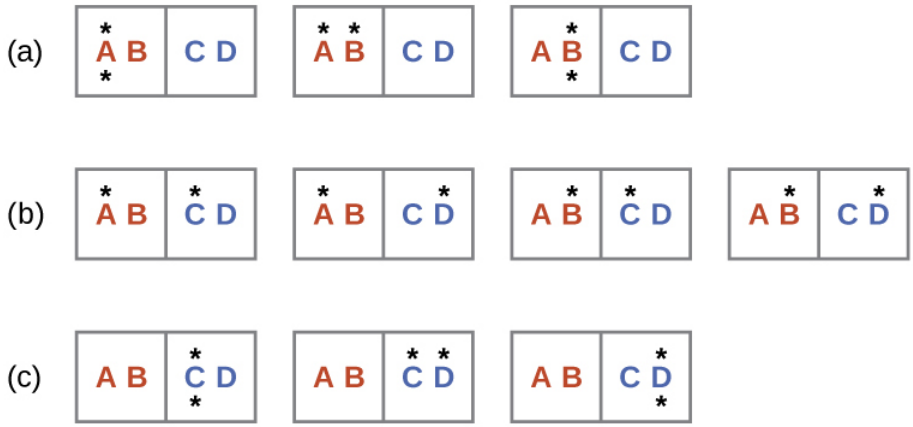
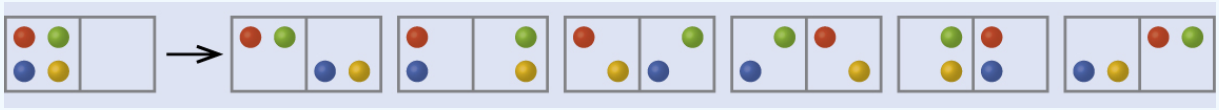


Figure **17.3.3**: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

✔ Example 17.3.1: Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23} J/K \times \ln \frac{6}{1} = 2.47 \times 10^{-23} J/K$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

? Exercise 17.3.1

Consider the system shown in Figure **17.3.3**. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure **17.3.4**. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

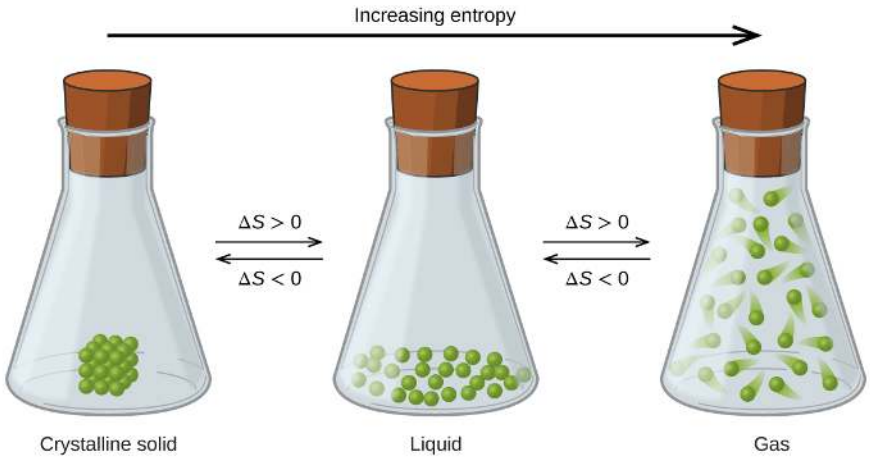


Figure **17.3.4**: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure **17.3.5**).

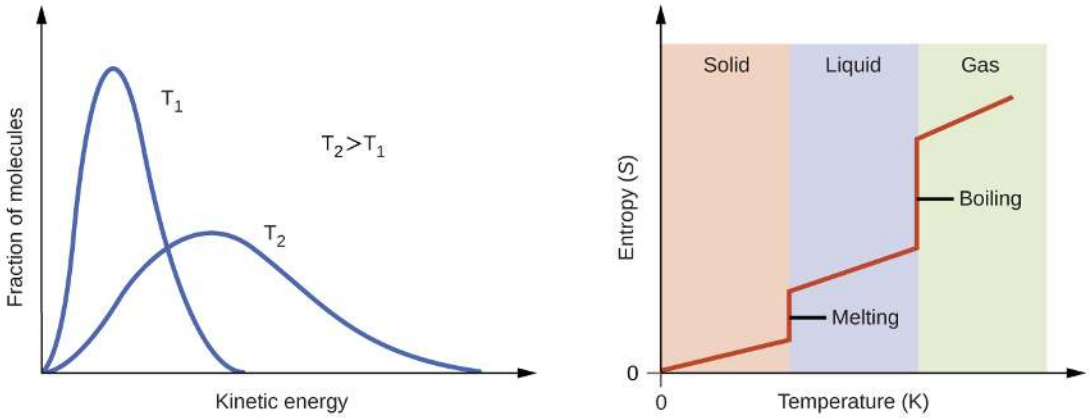


Figure **17.3.5**: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this simulator with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves 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 **17.3.2**.

Example 17.3.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature one mole liquid water at 50 °C
b. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
c. \(C_6 H_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. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 17.3.1

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

a. $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3^-(aq)$
b. the freezing of liquid water
c. $CO_2(s) \longrightarrow CO_2(g)$
d. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

Answer

(a) Positive; The solid dissolves to give an increase of mobile ions in solution.

(b) Negative; The liquid becomes a more ordered solid.

(c) Positive; The relatively ordered solid becomes a gas.

(d) Positive; There is a net increase in the amount of gaseous species.

This page titled 17.3: Entropy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **16.2: Entropy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

17.4: The Second and Third Laws of Thermodynamics

Learning Objectives

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

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{sys} = \frac{-q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{q_{rev}}{T_{surr}}$$

   The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

   $$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$
   $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{sys} = \frac{q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{-q_{rev}}{T_{surr}}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

   $$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$
   $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table **17.4.1**.

Table **17.4.1**: The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	at equilibrium

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example **17.4.1**.

Example 17.4.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$H_2O(s) \longrightarrow H_2O(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T} \\ &= 22.1 J/K + \frac{-6.00 \times 10^3 J}{263.15 K} = -0.7 J/K\end{aligned}$$

$S_{univ} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{sys} + \frac{q_{surr}}{T} \\ &= 22.1 J/K + \frac{-6.00 \times 10^3 J}{283.15 K} = +0.9 J/K\end{aligned}$$

$S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

Exercise 17.4.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

Entropy is a state function, so $\Delta S_{freezing} = -\Delta S_{melting}$ = −22.1 J/K and q_{surr} = +6.00 kJ. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0$$

This limiting condition for a system's entropy represents the third law of thermodynamics: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies** ($S°$) are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change** ($\Delta S°$) for a reaction may be computed using standard entropies as shown below:

$$\Delta S^\circ = \sum \nu S^\circ(\text{ products }) - \sum \nu S^\circ(\text{ reactants })$$

where ν represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°$ for the following reaction at room temperature

$$mA + nB \longrightarrow xC + yD$$

is computed as:

$$= [xS^\circ(C) + yS^\circ(D)] - [mS^\circ(A) + nS^\circ(B)]$$

A partial listing of standard entropies is provided in Table **17.4.2**, and additional values are provided in Appendix G. The example exercises that follow demonstrate the use of $S°$ values in calculating standard entropy changes for physical and chemical processes.

Table **17.4.2**: Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Substance	($J\ mol^{-1}\ K^{-1}$)
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
H(*g*)	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCI(*g*)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Example 17.4.2: Determination of $\Delta S°$

Calculate the standard entropy change for the following process:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S° = (1mol)\left(70.0Jmol^{-1}K^{-1}\right) - (1mol)\left(188.8Jmol^{-1}K^{-1}\right) = -118.8J/K$$

The value for $\Delta S°$ is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 17.4.2

Calculate the standard entropy change for the following process:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer

$-120.6\ J\ K^{-1}\ mol^{-1}$

Example 17.4.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S^\circ = \sum \nu S^\circ(\text{ products }) - \sum \nu S^\circ(\text{ reactants })$$

$$[2mol \times S^\circ(CO_2(g)) + 4mol \times S^\circ(H_2O(l))] - [2mol \times S^\circ(CH_3OH(l)) + 3mol \times S^\circ(O_2(g))]$$

$$= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\} = -161.6 J/K$$

Exercise 17.4.3

Calculate the standard entropy change for the following reaction:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer

24.7 J/K

This page titled 17.4: The Second and Third Laws of Thermodynamics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **16.3: The Second and Third Laws of Thermodynamics** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

17.5: Free Energy

Learning Objectives

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

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy** (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the free energy change (ΔG) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table **17.5.1** summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table **17.5.1**: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	moves spontaneously in the forward direction, as written, to reach equilibrium
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

What's "Free" about ΔG?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (w) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

$$\Delta G = \Delta H - T\Delta S$$

may be interpreted as representing the difference between the energy produced by the process, ΔH, and the energy lost to the surroundings, $T\Delta S$. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, ΔG. If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{max}$$

where w_{max} refers to all types of work except expansion (pressure-volume) work.

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., batteries) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done *on* the system to carry out the process.

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute **standard free energy changes**, ΔG^o, according to the following relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

It is important to understand that for phase changes, ΔG^o tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG^o tells you the **extent** of a reaction. In other words, ΔG^o for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^o < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^o > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

Example 17.5.1: Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG^o say about the spontaneity of this process?

Solution

The process of interest is the following:

$$\mathrm{H_2O\,(l)} \longrightarrow \mathrm{H_2O\,(g)}$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

From Appendix G:

Substance	ΔH_f°(kJ/mol)	S°(kJ/K mol)
$H_2O(l)$	−285.83	70.0
$H_2O(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ\left(\mathrm{H_2O\,(g)}\right) - \Delta H_f^\circ\left(\mathrm{H_2O\,(l)}\right)\\ &= [-241.82\ \mathrm{kJ/mol} - (-285.83)]\ \mathrm{kJ/mol} = 44.01\ \mathrm{kJ/mol}\\ \Delta S^\circ &= 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O\,(g)}\right) - 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O\,(l)}\right)\\ &= (1\ \mathrm{mol})\ 188.8 J/mol \cdot K - (1\ \mathrm{mol})\ 70.0\ \mathrm{J/mol\ K} = 118.8\ \mathrm{J\ /\ K}\\ \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\end{aligned}$$

Substitution into the standard free energy equation yields:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ &= 44.01\ \mathrm{kJ} - (298K \times 118.8\ \mathrm{J/K}) \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\\ &= 44.01\ \mathrm{kJ} - 35.4\ \mathrm{kJ}\\ &= 8.6\ \mathrm{kJ}\end{aligned}$$

At 298 K (25 °C) so boiling is nonspontaneous (*not* spontaneous).

? Exercise 17.5.1

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

$$\mathrm{C_2H_6\,(g)} \longrightarrow \mathrm{H_2\,(g) + C_2H_4\,(g)}$$

Answer

the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

The standard free energy change for a reaction may also be calculated from **standard free energy of formation** ΔG_f^o values of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpy of formation, ΔG_f^o is by definition zero for elemental substances in their standard states. The approach used to calculate ΔG^o for a reaction from ΔG_f^o values is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$mA + nB \longrightarrow xC + yD$$

the standard free energy change at room temperature may be calculated as

$$\begin{aligned}\Delta G^\circ &= \sum \nu \Delta G^\circ(\text{ products }) - \sum \nu \Delta G^\circ(\text{ reactants })\\ &= \left[x\Delta G_f^\circ(C) + y\Delta G_f^\circ(D)\right] - \left[m\Delta G_f^\circ(A) + n\Delta G_f^\circ(B)\right].\end{aligned}$$

✓ Example 17.5.2: Using Standard Free Energies of Formation to Calculate ΔG°

Consider the decomposition of yellow mercury(II) oxide.

\text is only supported in math mode

Calculate the standard free energy change at room temperature, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix G and are shown here.

Compound	ΔG_f°(kJ / mol)	ΔH_f°(kJ / mol)	S°(kJ / K mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ &= \sum \nu G_f^\circ(\text{ products }) - \sum \nu \Delta G_f^\circ(\text{ reactants }) \\ &= \left[1\Delta G_f^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta G_f^\circ\ \mathrm{O_2(g)}\right] - 1\Delta G_f^\circ\ \mathrm{HgO(s, yellow)} \\ &= \left[1\ \text{mol}(0\ \text{kJ / mol}) + \frac{1}{2}\ \text{mol}(0\ \text{kJ / mol})\right] - 1\ \text{mol}(-58.43\ \text{kJ / mol}) = 58.43\ \text{kJ / mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ &= \sum \nu \Delta H_f^\circ(\text{ products }) - \sum \nu \Delta H_f^\circ(\text{ reactants }) \\ &= \left[1\Delta H_f^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta H_f^\circ\ \mathrm{O_2(g)}\right] - 1\Delta H_f^\circ\ \mathrm{HgO(s, yellow)} \\ &= \left[1\ \text{mol}(0\ \text{kJ / mol}) + \frac{1}{2}\ \text{mol}(0\ \text{kJ / mol})\right] - 1\ \text{mol}(-90.46\ \text{kJ / mol}) = 90.46\ \text{kJ / mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum \nu \Delta S^\circ(\text{ products }) - \sum \nu \Delta S^\circ(\text{ reactants }) \\ &= \left[1\ \Delta S^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta S^\circ\ \mathrm{O_2(g)}\right] - 1\Delta S^\circ\ \mathrm{HgO(s, yellow)} \\ &= \left[1\ \text{mol}(75.9\ \text{J / mol K}) + \frac{1}{2}\ \text{mol}(205.2\ \text{J / mol K})\right] - 1\text{mol}(71.13\ \text{J / mol K}) \\ &= 107.4\ \ \text{J / mol K}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 90.46\ \text{kJ} - 298.15\ \text{K} \times 107.4\ \text{J / K} \cdot \text{mol} \times \frac{1\ \ \text{kJ}}{1000\ \text{J}} \\ &= (90.46 - 32.01)\ \text{kJ / mol} = 58.45\ \text{kJ / mol}\end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

? Exercise 17.5.1

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$\mathrm{C_2H_4(g)} \longrightarrow \mathrm{H_2(g) + C_2H_2(g)}$$

Answer

a. 140.8 kJ/mol, nonspontaneous
b. 141.5 kJ/mol, nonspontaneous

Free Energy Changes for Coupled Reactions

The use of free energies of formation to compute free energy changes for reactions as described above is possible because ΔG is a state function, and the approach is analogous to the use of Hess' Law in computing enthalpy changes (see the chapter on thermochemistry). Consider the vaporization of water as an example:

$$\mathrm{H_2O(l) \longrightarrow H_2O(g)}$$

An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:

$$\begin{array}{ll} \mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)} & \Delta G_f^\circ \text{ gas} \\ \mathrm{H_2O\,(l) \longrightarrow H_2\,(g) + \tfrac{1}{2}\,O_2\,(g)} & -\Delta G_f^\circ \text{ liquid} \\ \hline \mathrm{H_2O\,(l) \longrightarrow H_2O\,(g)} & \Delta G^\circ = \Delta G_f^\circ \text{ gas} - \Delta G_f^\circ \text{ liquid} \end{array}$$

This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction. For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for ΔG^o:

$$\mathrm{ZnS\,(s)} \rightarrow \mathrm{Zn\,(s) + S\,(s)} \quad \Delta G_1^\circ = 201.3kJ$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$\mathrm{S\,(s) + O_2\,(g)} \rightarrow \mathrm{SO_2\,(g)} \quad \Delta G_2^\circ = -300.1kJ$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$\mathrm{ZnS\,(s) + O_2\,(g)} \rightarrow \mathrm{Zn\,(s) + SO_2\,(g)}$$

$$\Delta G^\circ = 201.3\ \mathrm{kJ} + -300.1\ \mathrm{kJ} = -98.8\ \mathrm{kJ}$$

This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values is just an estimate. The gist of the calculation, however, holds true.

Example 17.5.3: Calculating Free Energy Change for a Coupled Reaction

Is a reaction coupling the decomposition of ZnS to the formation of $\mathrm{H_2S}$ expected to be spontaneous under standard conditions?

Solution

Following the approach outlined above and using free energy values from Appendix G:

$$\begin{array}{ll} \text{Decomposition of zinc sulfide:} & \mathrm{ZnS\,(s) \rightarrow Zn\,(s) + S\,(s)} \quad \Delta G_1^\circ = 201.3\ \mathrm{kJ} \\ \text{Formation of hydrogen sulfide:} & \mathrm{S\,(s) + H_2\,(g) \rightarrow H_2S\,(g)} \quad \Delta G_2^\circ = -33.4\ \mathrm{kJ} \\ \hline \text{Coupled reaction:} & \mathrm{ZnS\,(s) + H_2\,(g) \rightarrow Zn\,(s) + H_2S\,(g)} \quad \Delta G^\circ = 201.3\ \mathrm{kJ} + -33.4\ \mathrm{kJ} = 167.9\ \mathrm{kJ} \end{array}$$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

Exercise 17.5.3

What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?

$$\mathrm{FeS\,(s) + O_2\,(g)} \rightarrow \mathrm{Fe\,(s) + SO_2\,(g)}$$

Answer

−199.7 kJ; spontaneous

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

Note

The numerical value of ΔG^o is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG^o is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH^o and ΔS^o are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is greater than ΔH^o. If the $T\Delta S^o$ term is less than ΔH^o, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures.*
2. **Both ΔH^o and ΔS^o are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is less than ΔH^o. If the $T\Delta S^o$ term's magnitude is greater than ΔH^o, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures.*
3. **ΔH^o is positive and ΔS^o is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG^o will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures.*
4. **ΔH^o is negative and ΔS^o is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures.*

These four scenarios are summarized in Table **17.5.1**

Table **17.5.1**

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 17.5.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g)$$

Does the sign of ΔG° of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H^\circ < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^\circ > 0$). The reaction is therefore product-favored at equilibrium ($\Delta G^\circ < 0$) at all temperatures.

Exercise 17.5.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer

ΔH^o and ΔS^o are both negative; the reaction is product-favored at equilibrium at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of the sign of ΔG^o, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its ΔG^o) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG^o is plotted on the y axis versus T on the x axis:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$y = b + mx$$

Such a plot is shown in Figure 17.5.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of ΔG^o as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG^o) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG^o is zero:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Thus, saying a process is product-favored at equilibrium at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG^o for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of ΔG^o. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term ΔG^o to tell us the same information as the equilibrium constant, K. When ΔG^o < 0, K > 1, and the reaction will be product-favored at equilibrium. When ΔG^o > 0, K< 1, and the reaction is

reactant-favored at equilibrium. When $\Delta G^o = 0$, K =1, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and (essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^o < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^o > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^o = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔGº can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

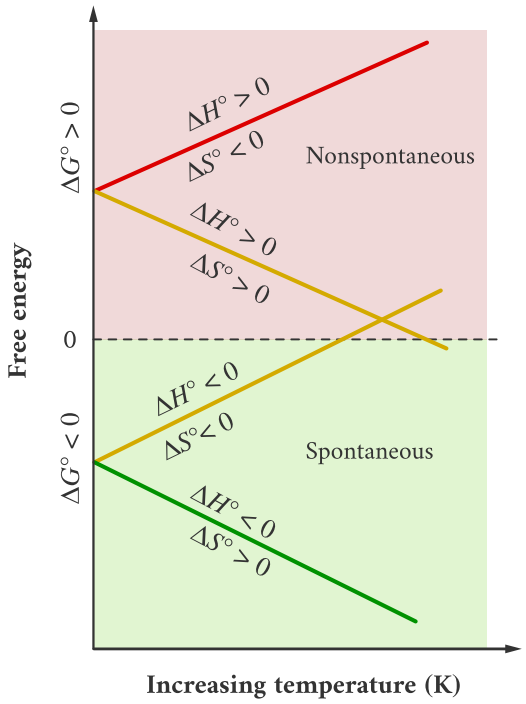


Figure **17.5.2**: These plots show the variation in ΔGº with temperature for the four possible combinations of arithmetic sign for ΔHº and ΔSº. Note that in this graph of ΔGº, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 17.5.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Tables T1 or T2,

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\mathrm{H_2O}(g)) - \Delta H_f^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(\mathrm{H_2O}(g)) - \Delta S_{298}^\circ(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

? Exercise 17.5.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K).

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for 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).

In the chapter on equilibrium the *reaction quotient*, Q, was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, K, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under *nonstandard conditions* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change according to this equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. For gas phase equilibria, the pressure-based reaction quotient, Q_P, is used. The concentration-based reaction quotient, Q_C, is used for condensed phase equilibria. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in Example 17.5.6.

Example 17.5.6: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here

$$2NH_3(g) \longrightarrow 3H_2(g) + N_2(g)$$

under the specified conditions?

- $T = 25°C$,
- $P_{N_2} = 0.870$ atm
- $P_{H_2} = 0.250$ atm
- $P_{NH_3} = 12.9$ atm

$$\Delta G° = 33.0 kJ/mol$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\begin{aligned} \Delta G &= \Delta G° + RT \ln Q \\ &= 33.0 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}} \times 298 K \times \ln \frac{(0.250^3) \times 0.870}{12.9^2} \right) \\ &= 9680 \frac{\text{J}}{\text{mol}} \text{ or } 9.68 \text{ kJ/mol} \end{aligned}$$

Since the computed value for Δ*G* is positive, the reaction is nonspontaneous under these conditions.

Exercise 17.5.6

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer

Δ*G* = –123.5 kJ/mol; yes

For a system at equilibrium, *Q* = *K* and Δ*G* = 0, and the previous equation may be written as

$$0 = \Delta G° + RT \ln K \quad \text{(at equilibrium)}$$

$$\Delta G° = -RT \ln K$$

or

$$K = e^{-\frac{\Delta G}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 17.5.2.

Table 17.5.2: Relations between Standard Free Energy Changes and Equilibrium Constants

K	Δ*G*°	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

Example 17.5.7: Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = [Ag^+]\,[Cl^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G^\circ &= \left[\Delta G_f^\circ\left(\mathrm{Ag^+(aq)}\right) + \Delta G_f^\circ\left(\mathrm{Cl^-(aq)}\right)\right] - \left[\Delta G_f^\circ(\mathrm{AgCl(s)})\right] \\ &= [77.1\ \mathrm{kJ/mol} - 131.2\ \mathrm{kJ/mol}] - [-109.8\ \mathrm{kJ/mol}] = 55.7\ \mathrm{kJ/mol}\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$\begin{aligned}K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} &= \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3 J/mol}{8.314 J/mol \cdot K \times 298.15 K}\right) \\ &= \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}\end{aligned}$$

This result is in reasonable agreement with the value provided in Appendix J.

Exercise 17.5.7

Use the thermodynamic data provided in Appendix G to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Answer

K = 3.1

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure **17.5.3**). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

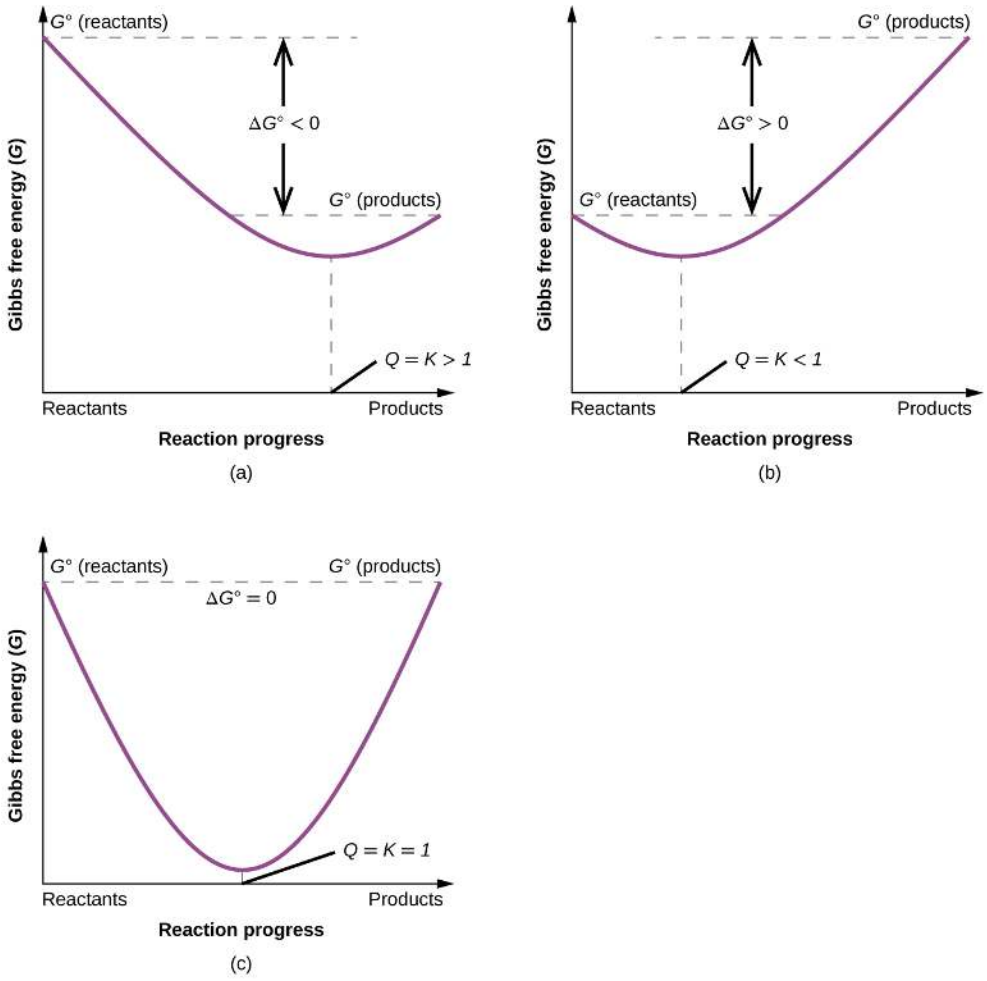


Figure **17.5.3**: These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

This page titled 17.5: Free Energy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **16.4: Free Energy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **16.4: Gibbs Energy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

17.6: Key Terms

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

Gibbs free energy change (*G*) | thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

microstate | possible configuration or arrangement of matter and energy within a system

nonspontaneous process | process that requires continual input of energy from an external source

reversible process | process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes

second law of thermodynamics | all spontaneous processes involve an increase in the entropy of the universe

spontaneous change | process that takes place without a continuous input of energy from an external source

standard entropy ($S°$) | entropy for one mole of a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K

standard entropy change ($\Delta S°$) | change in entropy for a reaction calculated using the standard entropies

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 free energy of formation | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

17.6: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **16.5: Key Terms** is licensed CC BY 4.0.

17.7: Key Equations

$$S = k \ln W$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta G = \Delta H - T\Delta S$$

17.7: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **16.6: Key Equations** is licensed CC BY 4.0.

17.8: Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system.

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system.

For a given substance, entropy depends on phase with $S_{solid} < S_{liquid} < S_{gas}$. For different substances in the same physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions and physical changes may be reliably predicted.

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is nonspontaneous, and if $\Delta S_{univ} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. A number of approaches to the computation of free energy changes are possible.

17.8: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **16.7: Summary** is licensed CC BY 4.0.

17.9: Exercises

1.

What is a spontaneous reaction?

2.

What is a nonspontaneous reaction?

3.

Indicate whether the following processes are spontaneous or nonspontaneous.

a. (f) Iron rusting in a moist atmosphere

4.

A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

5.

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.

6.

In Figure 16.8 all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

7.

In Figure 16.8 all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution (b) to distribution (d).

8.

How does the process described in the previous item relate to the system shown in Figure 16.4?

9.

Consider a system similar to the one in Figure 16.8, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to What does this comparison tell us about even larger systems?

10.

Consider the system shown in Figure 16.9. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

11.

Consider the system shown in Figure 16.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

12.

Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

a. $H_2(g)$, $HBrO_4(g)$, $HBr(g)$
b. $H_2O(l)$, $H_2O(g)$, $H_2O(s)$
c. $He(g)$, $Cl_2(g)$, $P_4(g)$

13.

At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

14.

14.

Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

15.

Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

a. $C_2H_5OH(l)$ or $C_3H_7OH(l)$
b. $C_2H_5OH(l)$ or $C_2H_5OH(g)$
c. $2H(g)$ or $H(g)$

16.

Predict the sign of the entropy change for the following processes.

a. An ice cube is warmed to near its melting point.
b. Exhaled breath forms fog on a cold morning.
c. Snow melts.

17.

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

a.
b.
c.

18.

Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

19.

Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

20.

What is the difference between ΔS and $\Delta S°$ for a chemical change?

21.

Calculate for the following changes.

a. (f)

22.

Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under the standard conditions to give gaseous carbon dioxide and liquid water.

23.

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

24.

“Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

25.

Using the relevant values listed in Appendix G, calculate for the following changes:

a.

b.

26.

From the following information, determine for the following:

27.

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

28.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

a. (f)

29.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

a. (f)

30.

What is the difference between ΔG and $\Delta G°$ for a chemical change?

31.

A reaction has = 100 kJ/mol and Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

32.

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

33.

Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. (f)

34.

Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. (f)

35.

Given:

a. Determine the standard free energy of formation, for phosphoric acid.
b. How does your calculated result compare to the value in Appendix G? Explain.

36.

Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

37.

Consider the decomposition of red mercury(II) oxide under standard state conditions.

a. Is the decomposition spontaneous under standard state conditions?

b. Above what temperature does the reaction become spontaneous?

38.

Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

a. Ammonia:
b. Diborane:
c. Hydrazine:
d. Hydrogen peroxide:

39.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. (f)

40.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. (f)

41.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a.
b.
c.
d.
e.

42.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a.
b.
c.
d.
e.

43.

Calculate the equilibrium constant at the temperature given.

a.
b.
c.
d.
e.

44.

Calculate the equilibrium constant at the temperature given.

a.
b.
c.
d.
e.

45.

Consider the following reaction at 298 K:

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

46.

Determine the normal boiling point (in kelvin) of dichloromethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

47.

Under what conditions is spontaneous?

48.

At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00 10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

49.

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

50.

Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

51.

In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

52.

Benzene can be prepared from acetylene. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

53.

Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

54.

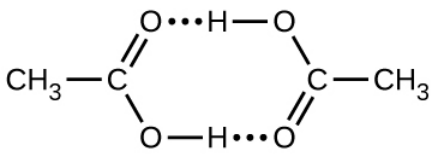
Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.

What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

55.

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3 10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

56.

Determine $\Delta G°$ for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

(b) Chlorine molecules dissociate according to this reaction:

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

57.

Given that the for $Pb^{2+}(aq)$ and $Cl^{-}(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

58.

Determine the standard free energy change, for the formation of $S^{2-}(aq)$ given that the for $Ag^{+}(aq)$ and $Ag_2S(s)$ are 77.1 kJ/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8 10^{-51}.

59.

Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

60.

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

a. Is the evaporation of water under standard thermodynamic conditions spontaneous?
b. Determine the equilibrium constant, K_P, for this physical process.
c. By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, is 0.011 atm.
d. If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of in the air?

61.

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

In this process, ATP becomes ADP summarized by the following equation:

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

62.

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

a. Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
b. Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

63.

Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

a.
b.

c.
d.

64.

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.

65.

An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

a. Determine for the decomposition of $Cu_2S(s)$.
b. The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine for the process.
c. The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

66.

What happens to (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

a.
b.
c.

This page titled 17.9: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **16.8: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

CHAPTER OVERVIEW

18: Electrochemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

18.1: Introduction
18.2: Summary
18.3: Exercises
18.4: Review of Redox Chemistry
18.5: Galvanic Cells
18.6: Electrode and Cell Potentials
18.7: Potential, Free Energy, and Equilibrium
18.8: Batteries and Fuel Cells
18.9: Corrosion
18.10: Electrolysis
18.11: Key Terms
18.12: Key Equations

This page titled 18: Electrochemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

18.1: Introduction

Another chapter in this text introduced the chemistry of reduction-oxidation (redox) reactions. This important reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred *indirectly* via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of *electrochemistry* has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (Figure 18.1.1). In this chapter, the essential concepts of electrochemistry will be addressed.



Figure 18.1.1: Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

18.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **17.0: Introduction** is licensed CC BY 4.0.

18.2: Summary

Redox reactions are defined by changes in reactant oxidation numbers, and those most relevant to electrochemistry involve actual transfer of electrons. Aqueous phase redox processes often involve water or its characteristic ions, H^+ and OH^-, as reactants in addition to the oxidant and reductant, and equations representing these reactions can be challenging to balance. The half-reaction method is a systematic approach to balancing such equations that involves separate treatment of the oxidation and reduction half-reactions.

Galvanic cells are devices in which a spontaneous redox reaction occurs indirectly, with the oxidant and reductant redox couples contained in separate half-cells. Electrons are transferred from the reductant (in the anode half-cell) to the oxidant (in the cathode half-cell) through an external circuit, and inert solution phase ions are transferred between half-cells, through a salt bridge, to maintain charge neutrality. The construction and composition of a galvanic cell may be succinctly represented using chemical formulas and others symbols in the form of a cell schematic (cell notation).

The property of potential, E, is the energy associated with the separation/transfer of charge. In electrochemistry, the potentials of cells and half-cells are thermodynamic quantities that reflect the driving force or the spontaneity of their redox processes. The cell potential of an electrochemical cell is the difference in between its cathode and anode. To permit easy sharing of half-cell potential data, the standard hydrogen electrode (SHE) is assigned a potential of exactly 0 V and used to define a single electrode potential for any given half-cell. The electrode potential of a half-cell, E_X, is the cell potential of said half-cell acting as a cathode when connected to a SHE acting as an anode. When the half-cell is operating under standard state conditions, its potential is the standard electrode potential, $E°_X$. Standard electrode potentials reflect the relative oxidizing strength of the half-reaction's reactant, with stronger oxidants exhibiting larger (more positive) $E°_X$ values. Tabulations of standard electrode potentials may be used to compute standard cell potentials, $E°_{cell}$, for many redox reactions. The arithmetic sign of a cell potential indicates the spontaneity of the cell reaction, with positive values for spontaneous reactions and negative values for nonspontaneous reactions (spontaneous in the reverse direction).

Potential is a thermodynamic quantity reflecting the intrinsic driving force of a redox process, and it is directly related to the free energy change and equilibrium constant for the process. For redox processes taking place in electrochemical cells, the maximum (electrical) work done by the system is easily computed from the cell potential and the reaction stoichiometry and is equal to the free energy change for the process. The equilibrium constant for a redox reaction is logarithmically related to the reaction's cell potential, with larger (more positive) potentials indicating reactions with greater driving force that equilibrate when the reaction has proceeded far towards completion (large value of K). Finally, the potential of a redox process varies with the composition of the reaction mixture, being related to the reactions standard potential and the value of its reaction quotient, Q, as described by the Nernst equation.

Galvanic cells designed specifically to function as electrical power supplies are called batteries. A variety of both single-use batteries (primary cells) and rechargeable batteries (secondary cells) are commercially available to serve a variety of applications, with important specifications including voltage, size, and lifetime. Fuel cells, sometimes called flow batteries, are devices that harness the energy of spontaneous redox reactions normally associated with combustion processes. Like batteries, fuel cells enable the reaction's electron transfer via an external circuit, but they require continuous input of the redox reactants (fuel and oxidant) from an external reservoir. Fuel cells are typically much more efficient in converting the energy released by the reaction to useful work in comparison to internal combustion engines.

Spontaneous oxidation of metals by natural electrochemical processes is called corrosion, familiar examples including the rusting of iron and the tarnishing of silver. Corrosion process involve the creation of a galvanic cell in which different sites on the metal object function as anode and cathode, with the corrosion taking place at the anodic site. Approaches to preventing corrosion of metals include use of a protective coating of zinc (galvanization) and the use of sacrificial anodes connected to the metal object (cathodic protection).

Nonspontaneous redox processes may be forced to occur in electrochemical cells by the application of an appropriate potential using an external power source—a process known as electrolysis. Electrolysis is the basis for certain ore refining processes, the industrial production of many chemical commodities, and the electroplating of metal coatings on various products. Measurement of the current flow during electrolysis permits stoichiometric calculations.

18.2: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **17.10: Summary** is licensed CC BY 4.0.

18.3: Exercises

1.

Identify each half-reaction below as either oxidation or reduction.

a.
b.
c.
d.

2.

Identify each half-reaction below as either oxidation or reduction.

a.
b.
c.
d.

3.

Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

a.
b.
c.
d.

4.

Balance the equations below assuming they occur in an acidic solution.

a.
b.
c.

5.

Identify the oxidant and reductant of each reaction of the previous exercise.

6.

Balance the equations below assuming they occur in a basic solution.

a.
b.
c.
d.

7.

Identify the oxidant and reductant of each reaction of the previous exercise.

8.

Why don’t hydroxide ions appear in equations for half-reactions occurring in acidic solution?

9.

Why don’t hydrogen ions appear in equations for half-reactions occurring in basic solution?

10.

Why must the charge balance in oxidation-reduction reactions?

11.

Write cell schematics for the following cell reactions, using platinum as an inert electrode as needed.

a.

b.

c.

d.

12.

Assuming the schematics below represent galvanic cells as written, identify the half-cell reactions occurring in each.

a.

b.

13.

Write a balanced equation for the cell reaction of each cell in the previous exercise.

14.

Balance each reaction below, and write a cell schematic representing the reaction as it would occur in a galvanic cell.

a.

b.

c.

d.

15.

Identify the oxidant and reductant in each reaction of the previous exercise.

16.

From the information provided, use cell notation to describe the following systems:

a. In one half-cell, a solution of $Pt(NO_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $Cu(NO_3)_2$ solution with all solute concentrations 1 *M*.
b. The cathode consists of a gold electrode in a 0.55 *M* $Au(NO_3)_3$ solution and the anode is a magnesium electrode in 0.75 *M* $Mg(NO_3)_2$ solution.
c. One half-cell consists of a silver electrode in a 1 *M* $AgNO_3$ solution, and in the other half-cell, a copper electrode in 1 *M* $Cu(NO_3)_2$ is oxidized.

17.

Why is a salt bridge necessary in galvanic cells like the one in Figure 17.3?

18.

An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

19.

An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

20.

The masses of three electrodes (A, B, and C), each from three different galvanic cells, were measured before and after the cells were allowed to pass current for a while. The mass of electrode A increased, that of electrode B was unchanged, and that of electrode C decreased. Identify each electrode as active or inert, and note (if possible) whether it functioned as anode or cathode.

21.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

a.

b.

c.
d.

22.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

a.
b.
c.
d.

23.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

24.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from a cathode half-cell consisting of a silver electrode in 1 *M* silver nitrate solution and an anode half-cell consisting of a zinc electrode in 1 *M* zinc nitrate. Is the reaction spontaneous at standard conditions?

25.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from an anode half-cell containing a cadmium electrode in 1 *M* cadmium nitrate and a cathode half-cell consisting of an aluminum electrode in 1 *M* aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

26.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

27.

For each pair of standard cell potential and electron stoichiometry values below, calculate a corresponding standard free energy change (kJ).

a. 0.000 V, n = 2
b. +0.434 V, n = 2
c. −2.439 V, n = 1

28.

For each pair of standard free energy change and electron stoichiometry values below, calculate a corresponding standard cell potential.

a. 12 kJ/mol, n = 3
b. −45 kJ/mol, n = 1

29.

Determine the standard cell potential and the cell potential under the stated conditions for the electrochemical reactions described here. State whether each is spontaneous or nonspontaneous under each set of conditions at 298.15 K.

a.
b. The cell made from an anode half-cell consisting of an aluminum electrode in 0.015 *M* aluminum nitrate solution and a cathode half-cell consisting of a nickel electrode in 0.25 *M* nickel(II) nitrate solution.
c. The cell comprised of a half-cell in which aqueous bromine (1.0 *M*) is being oxidized to bromide ion (0.11 *M*) and a half-cell in which Al^{3+} (0.023 *M*) is being reduced to aluminum metal.

30.

Determine ΔG and $\Delta G°$ for each of the reactions in the previous problem.

31.

Use the data in Appendix L to calculate equilibrium constants for the following reactions. Assume 298.15 K if no temperature is given.

a.
b.
c.
d.

32.

Consider a battery made from one half-cell that consists of a copper electrode in 1 *M* $CuSO_4$ solution and another half-cell that consists of a lead electrode in 1 *M* $Pb(NO_3)_2$ solution.

a. What is the standard cell potential for the battery?
b. What are the reactions at the anode, cathode, and the overall reaction?
c. Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.
d. Suppose sulfuric acid is added to the half-cell with the lead electrode and some $PbSO_4(s)$ forms. Would the cell potential increase, decrease, or remain the same?

33.

Consider a battery with the overall reaction:

a. What is the reaction at the anode and cathode?
b. A battery is “dead” when its cell potential is zero. What is the value of *Q* when this battery is dead?
c. If a particular dead battery was found to have $[Cu^{2+}] = 0.11$ *M*, what was the concentration of silver ion?

34.

Why do batteries go dead, but fuel cells do not?

35.

Use the Nernst equation to explain the drop in voltage observed for some batteries as they discharge.

36.

Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures.

37.

Which member of each pair of metals is more likely to corrode (oxidize)?

a. Mg or Ca
b. Au or Hg
c. Fe or Zn
d. Ag or Pt

38.

Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is an alloy composed mostly of iron, so use −0.447 V as the standard reduction potential for steel.

39.

Aluminum is more easily oxidized than iron and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. What might explain this observation?

40.

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.

41.

Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?

42.

Why would a sacrificial anode made of lithium metal be a bad choice

43.

If a 2.5 A current flows through a circuit for 35 minutes, how many coulombs of charge moved through the circuit?

44.

For the scenario in the previous question, how many electrons moved through the circuit?

45.

Write the half-reactions and cell reaction occurring during electrolysis of each molten salt below.

a. $CaCl_2$
b. LiH
c. $AlCl_3$
d. $CrBr_3$

46.

What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of 3.33 10^5 C passes through each cell?

47.

How long would it take to reduce 1 mole of each of the following ions using the current indicated?

a. Al^{3+}, 1.234 A
b. Ca^{2+}, 22.2 A
c. Cr^{5+}, 37.45 A
d. Au^{3+}, 3.57 A

48.

A current of 2.345 A passes through the cell shown in Figure 17.19 for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? (Hint: Is hydrogen the only gas present above the water?)

49.

An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a $Zn(NO_3)_2$ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm^3.

This page titled 18.3: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.11: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.4: Review of Redox Chemistry

Learning Objectives

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

- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Since reactions involving electron transfer are essential to the topic of electrochemistry, a brief review of redox chemistry is provided here that summarizes and extends the content of an earlier text chapter (see chapter on reaction stoichiometry). Readers wishing additional review are referred to the text chapter on reaction stoichiometry.

Oxidation Numbers

By definition, a redox reaction is one that entails changes in *oxidation number* (or *oxidation state*) for one or more of the elements involved. The oxidation number of an element in a compound is essentially an assessment of how the electronic environment of its atoms is different in comparison to atoms of the pure element. By this description, *the oxidation number of an atom in an element is equal to zero*. For an atom in a compound, *the oxidation number is equal to the charge the atom would have in the compound if the compound were ionic*. Consequential to these rules, *the sum of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule*. To illustrate this formalism, examples from the two compound classes, ionic and covalent, will be considered.

Simple ionic compounds present the simplest examples to illustrate this formalism, since by definition the elements' oxidation numbers are numerically equivalent to ionic charges. Sodium chloride, NaCl, is comprised of Na^+ cations and Cl^- anions, and so oxidation numbers for sodium and chlorine are, +1 and −1, respectively. Calcium fluoride, CaF_2, is comprised of Ca^{2+} cations and F^- anions, and so oxidation numbers for calcium and fluorine are, +2 and −1, respectively.

Covalent compounds require a more challenging use of the formalism. Water is a covalent compound whose molecules consist of two H atoms bonded separately to a central O atom via polar covalent O−H bonds. The shared electrons comprising an O−H bond are more strongly attracted to the more electronegative O atom, and so it acquires a partial negative charge in the water molecule (relative to an O atom in elemental oxygen). Consequently, H atoms in a water molecule exhibit partial positive charges compared to H atoms in elemental hydrogen. The sum of the partial negative and partial positive charges for each water molecule is zero, and the water molecule is neutral.

Imagine that the polarization of shared electrons within the O−H bonds of water were 100% complete—the result would be *transfer* of electrons from H to O, and water would be an ionic compound comprised of O^{2-} anions and H^+ cations. And so, the oxidations numbers for oxygen and hydrogen in water are −2 and +1, respectively. Applying this same logic to carbon tetrachloride, CCl_4, yields oxidation numbers of +4 for carbon and −1 for chlorine. In the nitrate ion, $\mathbf{NO_3^-}$, the oxidation number for nitrogen is +5 and that for oxygen is −2, summing to equal the 1− charge on the molecule:

$$(1N \text{ atom}) \left(\frac{+5}{N \text{ atom}} \right) + (3O \text{ atoms}) \left(\frac{-2}{O \text{ atom}} \right) = +5 + -6 = -1$$

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$\mathbf{NaCl\,(l) \longrightarrow Na\,(l) + Cl_2\,(g)} \qquad \textbf{(unbalanced)}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from −1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$\mathbf{2\,NaCl\,(l) \longrightarrow 2\,Na\,(l) + Cl_2\,(g)} \qquad \textbf{(balanced)}$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $H^+(aq)$ and $OH^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful.

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 H_2O.
4. Balance each half-reaction for H by adding 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 consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

Example 18.4.1: Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)} \\ &\text{reduction:} && \mathrm{HNO_3\,(aq) \longrightarrow NO\,(g)} \end{aligned}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)} \\ &\text{reduction:} && \mathrm{HNO_3\,(aq) \longrightarrow NO\,(g)} \end{aligned}$$

Step 3: Balance each half-reaction for O by adding H_2O.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)} \\ &\text{reduction:} && \mathrm{HNO_3\,(aq) \longrightarrow NO\,(g) + 2H2O\,(l)} \end{aligned}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)} \\ &\text{reduction:} && \mathrm{3H^+\,(aq) + HNO_3\,(aq) \longrightarrow NO\,(g) + 2\,H_2O\,(l)} \end{aligned}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq) + 2e^-} \\ &\text{reduction:} && \mathrm{3e^- + 3\,H^+\,(aq) + HNO_3\,(aq) \longrightarrow NO\,(g) + 2\,H_2O\,(l)} \end{aligned}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

$$\text{oxidation } (\times 3): \quad 3\ Cu(s) \longrightarrow 3\ Cu^{2+}(aq) + 6\ \cancel{2}\ e^-$$
$$\text{reduction } (\times 2): \quad 6\ \cancel{3}\ e^- + 6\ \cancel{3}\ H^+(aq) + 2\ HNO_3(aq) \longrightarrow 2\ NO(g) + 4\ \cancel{2}\ H_2O(l)$$

Step 7: Add the two half-reactions and simplify.

$$3\,Cu(s) + \cancel{6e^-} + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + \cancel{6e^-} + 2\,NO(g) + 4\,H_2O(l)$$
$$3\,Cu(s) + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)$$

Step 8: If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$3\,Cu(s) + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)$$

? Exercise 18.4.1

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

Answer

$$Cu(s) + 2\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow Cu^{2+}(aq) + 2\,NO_2(g) + 2\,H_2O(l)$$

✔ Example 18.4.2: Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, , and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion, The reaction takes place in a basic solution.

Solution

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad Cr(OH)_3(s) \longrightarrow {CrO_4}^{2-}(aq)$$
$$\text{reduction:} \quad {MnO_4}^-(aq) \longrightarrow MnO_2(s)$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad Cr(OH)_3(s) \longrightarrow {CrO_4}^{2-}(aq)$$
$$\text{reduction:} \quad {MnO_4}^-(aq) \longrightarrow MnO_2(s)$$

Step 3: Balance each half-reaction for O by adding H_2O.

$$\text{oxidation:} \quad \mathbf{H2O(l)} + Cr(OH)_3(s) \longrightarrow {CrO_4}^{2-}(aq)$$
$$\text{reduction:} \quad {MnO_4}^-(aq) \longrightarrow MnO_2(s) + \mathbf{2H2O(l)}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\text{oxidation:} \quad H_2O(l) + Cr(OH)_3(s) \longrightarrow {CrO_4}^{2-}(aq) + \mathbf{5H^+(aq)}$$
$$\text{reduction:} \quad \mathbf{4H^+(aq)} + {MnO_4}^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad H_2O(l) + Cr(OH)_3(s) \longrightarrow {CrO_4}^{2-}(aq) + 5\,H^+(aq) + \mathbf{3e^-}$$
$$\text{reduction:} \quad \mathbf{3e^-} + 4\,H^+(aq) + {MnO_4}^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

This step is not necessary since the number of electrons is already in balance.

Step 7: Add the two half-reactions and simplify.

$$\begin{aligned} &\cancel{H2O(l)} + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + \cancel{5}^{1}H^+(aq) + \cancel{3e^-} \\ + \quad &\cancel{3e^-} + \cancel{4H^+(aq)} + MnO_4^-(aq) \longrightarrow MnO_2(s) + \cancel{2}^{1}H_2O(l) \\ \hline &Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H^+(aq) + H_2O(l) \end{aligned}$$

Step 8: If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

$$\begin{aligned} &OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) \\ &\quad + \cancel{H^+(aq)} + H_2O(l) + \cancel{OH^-(aq)} \end{aligned}$$

after neutralizing the H^+, we get the balanced equation for the reaction in a basic solution

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2H_2O(l)$$

Exercise 18.4.2

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, BrO_3^-. Write the balanced equation for this reaction occurring in a basic medium.

Answer

$$H_2O(l) + 2MnO_4^-(aq) + Br^-(aq) \longrightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

This page titled 18.4: Review of Redox Chemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.1: Review of Redox Chemistry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.5: Galvanic Cells

Learning Objectives

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

- Describe the function of a galvanic cell and its components
- Use cell notation to symbolize the composition and construction of galvanic cells

As demonstration of spontaneous chemical change, Figure **18.5.1**: shows the result of immersing a coiled wire of copper into an aqueous solution of silver nitrate. A gradual but visually impressive change spontaneously occurs as the initially colorless solution becomes increasingly blue, and the initially smooth copper wire becomes covered with a porous gray solid.

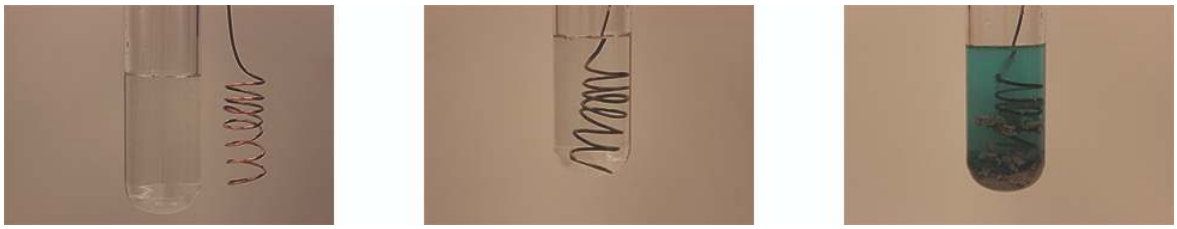


Figure **18.5.1**: A copper wire and an aqueous solution of silver nitrate (left) are brought into contact (center) and a spontaneous transfer of electrons occurs, creating blue $Cu^{2+}(aq)$ and gray Ag(*s*) (right).

These observations are consistent with (i) the oxidation of elemental copper to yield copper(II) ions, $Cu^{2+}(aq)$, which impart a blue color to the solution, and (ii) the reduction of silver(I) ions to yield elemental silver, which deposits as a fluffy solid on the copper wire surface. And so, *the direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous* under the employed conditions. A summary of this redox system is provided by these equations:

Consider the construction of a device that contains all the reactants and products of a redox system like the one here, but prevents physical contact between the reactants. Direct transfer of electrons is, therefore, prevented; transfer, instead, takes place indirectly through an external circuit that contacts the separated reactants. Devices of this sort are generally referred to as *electrochemical cells*, and those in which a spontaneous redox reaction takes place are called galvanic cells (or voltaic cells).

A galvanic cell based on the spontaneous reaction between copper and silver(I) is depicted in Figure **18.5.2**. The cell is comprised of two half-cells, each containing the redox conjugate pair (“couple”) of a single reactant. The half-cell shown at the left contains the Cu(0)/Cu(II) couple in the form of a solid copper foil and an aqueous solution of copper nitrate. The right half-cell contains the Ag(I)/Ag(0) couple as solid silver foil and an aqueous silver nitrate solution. An external circuit is connected to each half-cell at its solid foil, meaning the Cu and Ag foil each function as an *electrode*. By definition, the anode of an electrochemical cell is the electrode at which oxidation occurs (in this case, the Cu foil) and the cathode is the electrode where reduction occurs (the Ag foil). The redox reactions in a galvanic cell occur only at the interface between each half-cell’s reaction mixture and its electrode. To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a salt bridge. The spontaneous reaction in this cell produces Cu^{2+} cations in the anode half-cell and consumes Ag^{+} ions in the cathode half-cell, resulting in a compensatory flow of inert ions from the salt bridge that maintains charge balance. Increasing concentrations of Cu^{2+} in the anode half-cell are balanced by an influx of NO_3^- from the salt bridge, while a flow of Na^{+} into the cathode half-cell compensates for the decreasing Ag^{+} concentration.

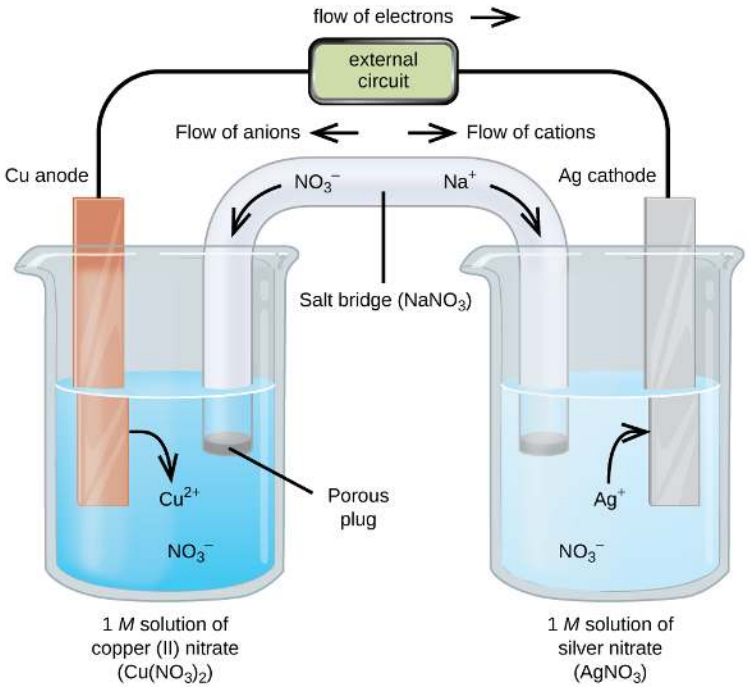


Figure 18.5.2: A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.

Cell Notation

Abbreviated symbolism is commonly used to represent a galvanic cell by providing essential information on its composition and structure. These symbolic representations are called cell notations or cell schematics, and they are written following a few guidelines:

- The relevant components of each half-cell are represented by their chemical formulas or element symbols
- All interfaces between component phases are represented by vertical parallel lines; if two or more components are present in the same phase, their formulas are separated by commas
- By convention, the schematic begins with the anode and proceeds left-to-right identifying phases and interfaces encountered within the cell, ending with the cathode

A verbal description of the cell as viewed from anode-to-cathode is often a useful first-step in writing its schematic. For example, the galvanic cell shown in Figure 18.5.2: consists of a solid copper anode immersed in an aqueous solution of copper(II) nitrate that is connected via a salt bridge to an aqueous silver(I) nitrate solution, immersed in which is a solid silver cathode. Converting this statement to symbolism following the above guidelines results in the cell schematic:

Consider a different galvanic cell (see Figure 18.5.3) based on the spontaneous reaction between solid magnesium and aqueous iron(III) ions:

In this cell, a solid magnesium anode is immersed in an aqueous solution of magnesium chloride that is connected via a salt bridge to an aqueous solution containing a mixture of iron(III) chloride and iron(II) chloride, immersed in which is a platinum cathode. The cell schematic is then written as

Notice the cathode half-cell is different from the others considered thus far in that its electrode is comprised of a substance (Pt) that is neither a reactant nor a product of the cell reaction. This is required when neither member of the half-cell's redox couple can reasonably function as an electrode, which must be electrically conductive and in a phase separate from the half-cell solution. In this case, both members of the redox couple are solute species, and so Pt is used as an inert electrode that can simply provide or accept electrons to redox species in solution. Electrodes constructed from a member of the redox couple, such as the Mg anode in this cell, are called active electrodes.

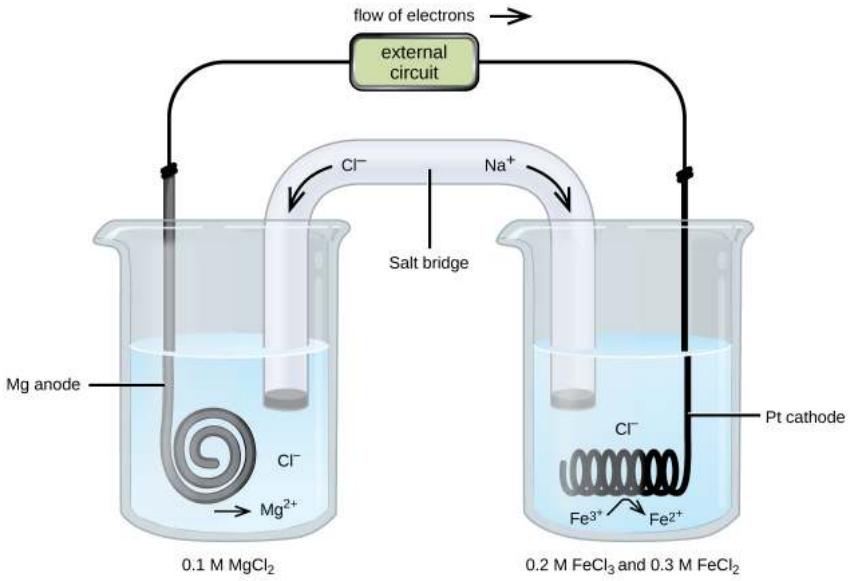


Figure **18.5.3**: A galvanic cell based on the spontaneous reaction between magnesium and iron(III) ions.

Example 18.5.1: Writing Galvanic Cell Schematics

A galvanic cell is fabricated by connecting two half-cells with a salt bridge, one in which a chromium wire is immersed in a 1 M $CrCl_3$ solution and another in which a copper wire is immersed in 1 M $CuCl_2$. Assuming the chromium wire functions as an anode, write the schematic for this cell along with equations for the anode half-reaction, the cathode half-reaction, and the overall cell reaction.

Solution

Since the chromium wire is stipulated to be the anode, the schematic begins with it and proceeds left-to-right, symbolizing the other cell components until ending with the copper wire cathode:

The half-reactions for this cell are

Multiplying to make the number of electrons lost by Cr and gained by Cu^{2+} equal yields

Adding the half-reaction equations and simplifying yields an equation for the cell reaction:

Exercise 18.5.1

Omitting solute concentrations and spectator ion identities, write the schematic for a galvanic cell whose net cell reaction is shown below.

Answer

This page titled 18.5: Galvanic Cells is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.2: Galvanic Cells** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.6: Electrode and Cell Potentials

Learning Objectives

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

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Unlike the spontaneous oxidation of copper by aqueous silver(I) ions described previously, immersing a copper wire in an aqueous solution of lead(II) ions yields no reaction. The two species, $Ag^+(aq)$ and $Pb^{2+}(aq)$, thus show a distinct difference in their redox activity towards copper: the silver ion spontaneously oxidized copper, but the lead ion did not. Electrochemical cells permit this relative redox activity to be quantified by an easily measured property, *potential*. This property is more commonly called *voltage* when referenced in regard to electrical applications, and it is a measure of energy accompanying the transfer of charge. Potentials are measured in the volt unit, defined as one joule of energy per one coulomb of charge, V = J/C.

When measured for purposes of electrochemistry, a potential reflects the driving force for a specific type of charge transfer process, namely, the transfer of electrons between redox reactants. Considering the nature of potential in this context, it is clear that the potential of a single half-cell or a single electrode can't be measured; "transfer" of electrons requires both a donor and recipient, in this case a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called cell potentials, E_{cell}, defined as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

where $E_{cathode}$ and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts. As for other thermodynamic quantities, the standard cell potential, $E°_{cell}$, is a cell potential measured when both half-cells are under standard-state conditions (1 *M* concentrations, 1 bar pressures, 298 K):

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0 V. This half-cell is the **standard hydrogen electrode** (SHE) and it is based on half-reaction below:

$$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$$

A typical SHE contains an inert platinum electrode immersed in precisely 1 *M* aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K (see Figure 18.6.1).

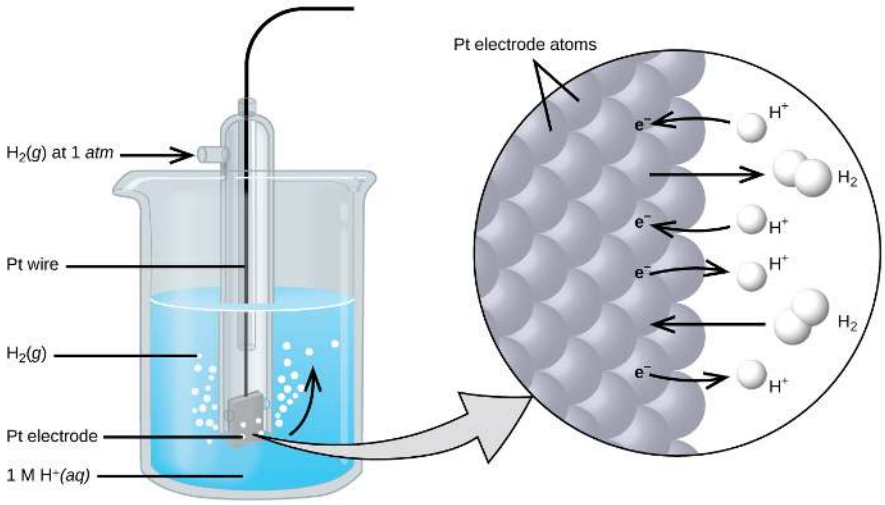


Figure **18.6.1**: A standard hydrogen electrode (SHE).

The assigned potential of the SHE permits the definition of a conveniently measured potential for a single half-cell. The electrode potential (E_X) for a half-cell *X* is defined as *the potential measured for a cell comprised of X acting as cathode and the SHE acting as anode*:

$$E_{\text{cell}} = E_X - E_{SHE}$$
$$E_{SHE} = 0V \text{ (defined)}$$
$$E_{\text{cell}} = E_X$$

When the half-cell *X* is under standard-state conditions, its potential is the standard electrode potential, $E°_X$. Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called *standard reduction potentials*.

This approach to measuring electrode potentials is illustrated in Figure **18.6.2**: , which depicts a cell comprised of an SHE connected to a copper(II)/copper(0) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections insure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V is measured, and so

$$E°_{\text{cell}} = E°_{\text{Cu}} = +0.337V$$

Tabulations of E° values for other half-cells measured in a similar fashion are available as reference literature to permit calculations of cell potentials and the prediction of the spontaneity of redox processes.

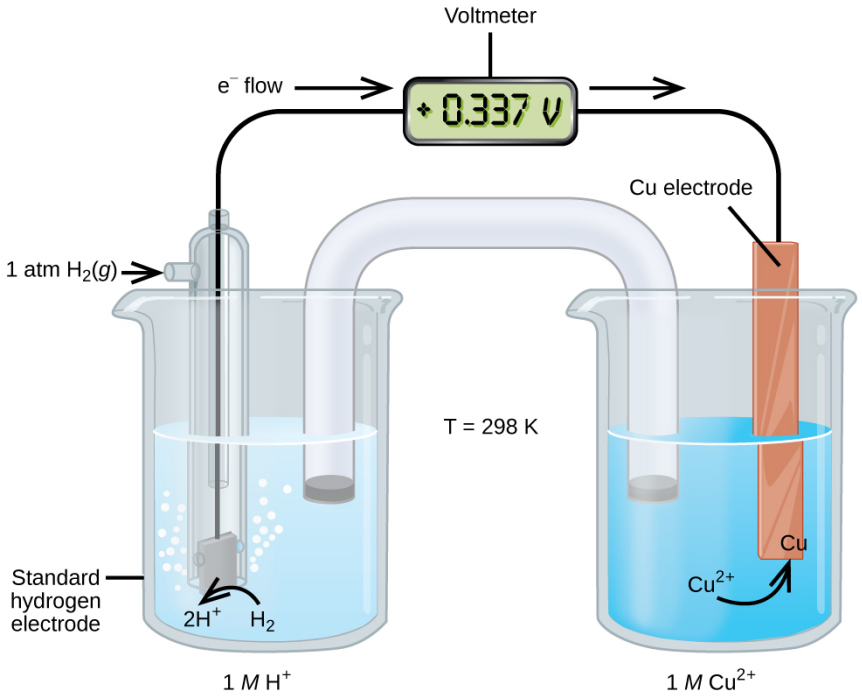


Figure **18.6.2**: A cell permitting experimental measurement of the standard electrode potential for the half-reaction

Table **18.6.1** provides a listing of standard electrode potentials for a selection of half-reactions in numerical order, and a more extensive alphabetical listing is given in Appendix L.

Table **18.6.1**: Selected Standard Reduction Potentials at 25 °C

https://chem.libretexts.org/@go/page/548619

Half-Reaction	$E°$ (V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.1262
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.1375
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.257
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.3505
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.4030
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.447
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.744
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	-1.185
$Zn(OH)_2(s) + 2e^- \longrightarrow Zn(s) + 2OH^-(aq)$	-1.245
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.7618
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.662
$Mg_2(aq) + 2e^- \longrightarrow Mg(s)$	-2.372
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71

Half-Reaction	$E°$ (V)
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.868
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.912
$K^+(aq) + e^- \longrightarrow K(s)$	-2.931
$K^+(aq) + e^- \longrightarrow K(s)$	-3.04

Example 18.6.1: Calculating Standard Cell Potentials

What is the standard potential of the galvanic cell shown in Figure 17.3?

Solution

The cell in Figure 17.3 is galvanic, the spontaneous cell reaction involving oxidation of its copper anode and reduction of silver(I) ions at its silver cathode:

$$\begin{array}{ll} \textbf{anode:} & Cu(s) \longrightarrow Cu^{2+} + 2e^- \\ \textbf{cathode:} & 2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s) \\ \hline \textbf{cell:} & Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+} + 2Ag(s) \qquad E^o_{cell} = 0\,V \end{array}$$

The standard cell potential computed as

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{Ag} - E^\circ_{Cu} \\ &= 0.7996V - 0.34V \\ &= +0.46V \end{aligned}$$

18.6.1 Exercise

What is the standard cell potential expected if the silver cathode half-cell in Figure 17.3 is replaced with a lead half-cell:

$$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$$

Answer

−0. 47 V

Intrepreting Electrode and Cell Potentials

Thinking carefully about the definitions of cell and electrode potentials and the observations of spontaneous redox change presented thus far, a significant relation is noted. The previous section described the spontaneous oxidation of copper by aqueous silver(I) ions, but no observed reaction with aqueous lead(II) ions. Results of the calculations in Example **18.6.1** have just shown *the spontaneous process is described by a positive cell potential* while *the nonspontaneous process exhibits a negative cell potential*. And so, with regard to the relative effectiveness ("strength") with which aqueous Ag^+ and Pb^{2+} ions oxidize Cu under standard conditions, *the stronger oxidant is the one exhibiting the greater standard electrode potential*, $E°$. Since by convention electrode potentials are for reduction processes, an increased value of E^o corresponds to an increased driving force behind the reduction of the species (hence increased effectiveness of its action as an *oxidizing agent* on some other species). Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE, indicating the reactant of the half-reaction is a weaker oxidant than aqueous hydrogen ions.

Applying this logic to the numerically ordered listing of standard electrode potentials in Table **18.6.1** shows this listing to be likewise in order of the oxidizing strength of the half-reaction's reactant species, decreasing from strongest oxidant (most positive $E°$) to weakest oxidant (most negative $E°$). Predictions regarding the spontaneity of redox reactions under standard state conditions can then be easily made by simply comparing the relative positions of their table entries. By definition, $E°_{cell}$ is positive when

$E^{o}_{\text{cathode}} > E^{o}_{\text{anode}}$, and so any redox reaction in which the oxidant's entry is above the reductant's entry is predicted to be spontaneous.

Reconsideration of the two redox reactions in Example **18.6.1** provides support for this fact. The entry for the silver(I)/silver(0) half-reaction is above that for the copper(II)/copper(0) half-reaction, and so the oxidation of Cu by Ag^{+} is predicted to be spontaneous ($E°_{\text{cathode}} > E°_{\text{anode}}$ and so $E°_{\text{cell}} > 0$). Conversely, the entry for the lead(II)/lead(0) half-cell is beneath that for copper(II)/copper(0), and the oxidation of Cu by Pb^{2+} is nonspontaneous ($E°_{\text{cathode}} < E°_{\text{anode}}$ and so $E°_{\text{cell}} < 0$).

Recalling the chapter on thermodynamics, the spontaneities of the forward and reverse reactions of a reversible process show a reciprocal relationship: if a process is spontaneous in one direction, it is non-spontaneous in the opposite direction. As an indicator of spontaneity for redox reactions, the potential of a cell reaction shows a consequential relationship in its arithmetic sign. The spontaneous oxidation of copper by lead(II) ions is *not* observed,

$$\mathrm{Cu\,(s) + Pb^{2+}\,(aq) \longrightarrow Cu^{2+}\,(aq) + Pb\,(s)} \quad E^{\circ}_{\text{forward}} = -0.47\ \mathrm{V (negative, non-spontaneous)}$$

and so the reverse reaction, the oxidation of lead by copper(II) ions, is predicted to occur spontaneously:

$$\mathrm{Pb\,(s) + Cu^{2+}\,(aq) \longrightarrow Pb^{2+}\,(aq) + Cu\,(s)} \quad E^{\circ}_{\text{forward}} = +0.47\ \mathrm{V (positive, spontaneous)}$$

Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions, and so the cell potential is calculated from electrode potentials in the reverse subtraction order than that for the forward reaction. In practice, a voltmeter would report a potential of −0.47 V with its red and black inputs connected to the Pb and Cu electrodes, respectively. If the inputs were swapped, the reported voltage would be +0.47 V.

✔ Example 18.6.2: Predicting Redox Spontaneity

Are aqueous iron(II) ions predicted to spontaneously oxidize elemental chromium under standard state conditions? Assume the half-reactions to be those available in Table **18.6.1**.

Solution

Referring to the tabulated half-reactions, the redox reaction in question can be represented by the equations below:

$$\mathrm{Cr\,(s) + Fe^{2+}\,(aq) \longrightarrow Cr^{3+}\,(aq) + Fe\,(s)}$$

The entry for the putative oxidant, Fe^{2+}, appears *above* the entry for the reductant, Cr, and so a spontaneous reaction is predicted per the quick approach described above. Supporting this predication by calculating the standard cell potential for this reaction gives

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= E^{\circ}_{\text{Fe(II)}} - E^{\circ}_{\text{Cr}} \\ &= -0.447V - -0.744V = +0.297V \end{aligned}$$

The positive value for the standard cell potential indicates the process is spontaneous under standard state conditions.

18.6.2? Exercise

Use the data in Table **18.6.1** to predict the spontaneity of the oxidation of bromide ion by molecular iodine under standard state conditions, supporting the prediction by calculating the standard cell potential for the reaction. Repeat for the oxidation of iodide ion by molecular bromine.

Answer

$$\begin{aligned} \mathrm{I_2\,(s) + 2\,Br^-\,(aq) \longrightarrow 2\,I^-\,(aq) + Br_2\,(l)} \quad & E_{\text{cell}} = -0.5518\ \mathrm{V\ (nonspontaneous)} \\ \mathrm{Br_2\,(s) + 2\,I^-\,(aq) \longrightarrow 2\,Br^-\,(aq) + I_2\,(l)} \quad & E^{\circ}_{\text{cell}} = +0.5518\ \mathrm{V\ (spontaneous)} \end{aligned}$$

This page titled 18.6: Electrode and Cell Potentials is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.3: Electrode and Cell Potentials** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.7: Potential, Free Energy, and Equilibrium

Learning Objectives

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

- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

So far in this chapter, the relationship between the cell potential and reaction *spontaneity* has been described, suggesting a link to the free energy change for the reaction (see chapter on thermodynamics). The interpretation of potentials as measures of oxidant *strength* was presented, bringing to mind similar measures of acid-base strength as reflected in equilibrium constants (see the chapter on acid-base equilibria). This section provides a summary of the relationships between potential and the related thermodynamic properties ΔG and K.

E° and ΔG°

The standard free energy change of a process, $\Delta G°$, was defined in a previous chapter as the maximum work that could be performed by a system, w_{max}. In the case of a redox reaction taking place within a galvanic cell under standard state conditions, essentially all the work is associated with transferring the electrons from reductant-to-oxidant, w_{elec}:

$$\Delta G° = w_{\text{max}} = w_{\text{elec}}$$

The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\Delta G° = w_{\text{elec}} = -nFE°_{\text{cell}}$$

where n is the number of moles of electrons transferred, F is **Faraday's constant**, and $E°_{cell}$ is the standard cell potential. The relation between free energy change and standard cell potential confirms the sign conventions and spontaneity criteria previously discussed for both of these properties: spontaneous redox reactions exhibit positive potentials and negative free energy changes.

E° and K

Combining a previously derived relation between ΔG° and K (see the chapter on thermodynamics) and the equation above relating ΔG° and $E°_{\text{cell}}$ yields the following:

$$\Delta G° = -RT \ln K = -nFE°_{\text{cell}} \tag{18.7.1}$$

with

$$E°_{\text{coll}} = \left(\frac{RT}{nF}\right) \ln K$$

This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product. A summary of the relations between $E°$, $\Delta G°$ and K is depicted in Figure 18.7.1, and a table correlating reaction spontaneity to values of these properties is provided in Table 18.7.1.

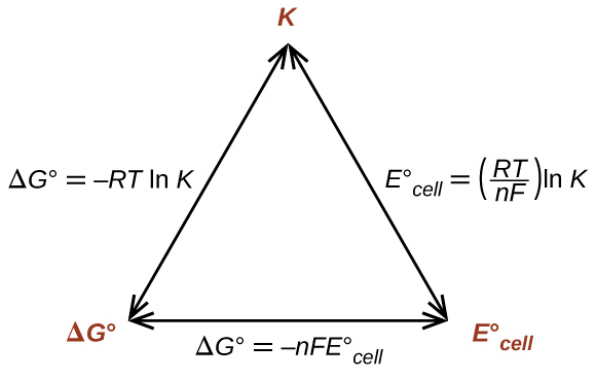


Figure 18.7.1: Graphic depicting the relation between three important thermodynamic properties.

Table 18.7.1

K	$\Delta G°$	$E°_{cell}$	Comment
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
= 1	= 0	= 0	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

Example 18.7.1: Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

Use data from Appendix L to calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction and the composition of an equilibrium mixture of reactants and products.

$$2\,Ag^+(aq) + Fe(s) \rightleftharpoons 2\,Ag(s) + Fe^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Appendix L.

anode:	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-$	$E^o_{Fe^{2+}/Fe} = -0.447\,V$
cathode:	$2 \times (Ag^+(aq) + e^- \longrightarrow Ag(s))$	$E^o_{Ag^+/Ag} = +0.7996\,V$
cell:	$Fe(s) + 2\,Ag^+(aq) \longrightarrow Fe^{2+}(aq) + 2\,Ag(s)$	$E^o_{cell} = +1.2247\,V$

with

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^o_{Fe^{2+}/Fe} - E^o_{Ag^+/Ag} = +1.2247\,V$$

With $n = 2$, the equilibrium constant is then

$$E^\circ_{cell} = \frac{0.0592V}{n} \log K$$

$$K = 10^{n \times E^\circ_{cal}/0.0592V}$$

$$= 10^{2 \times 1.247V/0.0592V}$$

$$= 10^{42.128}$$

$$= 1.3 \times 10^{42}$$

The standard free energy is then Equation 18.7.1

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$= -2 \times 96,485 \frac{C}{mol} \times 1.247 \frac{J}{C} = -240.6 \frac{kJ}{mol}$$

The reaction is spontaneous, as indicated by a negative free energy change and a positive cell potential. The *K* value is very large, indicating the reaction proceeds to near completion to yield an equilibrium mixture containing mostly products.

? Exercise 18.7.1

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$Sn(s) + 2\,Cu^{2+}(aq) \rightleftharpoons Sn^{2+}(aq) + 2\,Cu^{+}(aq)$$

Answer

Spontaneous

$n = 2$

$E^\circ_{cell} = +0.291V$

$[\Delta G^\circ = -56.2 \frac{kJ}{mol}$

K = 6.8 10^9.

Potentials at Nonstandard Conditions: The Nernst Equation

Most of the redox processes that interest science and society do not occur under standard state conditions, and so the potentials of these systems under nonstandard conditions are a property worthy of attention. Having established the relationship between potential and free energy change in this section, the previously discussed relation between free energy change and reaction mixture composition can be used for this purpose.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Notice the reaction quotient, *Q*, appears in this equation, making the free energy change dependent upon the composition of the reaction mixture. Substituting the equation relating free energy change to cell potential yields the **Nernst equation**:

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln Q$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

This equation describes how the potential of a redox system (such as a galvanic cell) varies from its standard state value, specifically, showing it to be a function of the number of electrons transferred, *n*, the temperature, *T*, and the reaction mixture composition as reflected in *Q*. A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and standard temperature (298) K), along with a factor converting from natural to base-10 logarithms, have been included:

$$E_{cell} = E^\circ_{cell} - \frac{0.0592V}{n} \log Q \tag{18.7.2}$$

Example 18.7.2: Predicting Redox Spontaneity Under Nonstandard Conditions

Use the Nernst equation to predict the spontaneity of the redox reaction shown below at room temperature.

$$\mathrm{Co(s) + Fe^{2+}(aq,\ 1.94\ M) \longrightarrow Co^{2+}(aq,\ 0.15\ M) + Fe(s)}$$

Solution

Collecting information from Appendix L and the problem,

anode:	$\mathrm{Co(s) \longrightarrow Co^{2+}(aq) + 2e^-}$	$E^o_{\mathrm{Co^{2+}/Co}} = -0.28\,\mathrm{V}$
cathode:	$\mathrm{Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)}$	$E^o_{\mathrm{Fe^{+}/Fe}} = -0.447\,\mathrm{V}$
cell:	$\mathrm{Co(s) + Fe^{2+}(Aq) \longrightarrow Fe(s) + Co^{2+}(aq)}$	$E^o_{\mathrm{cell}} = -0.17\,\mathrm{V}$

with

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} = -0.447V - (-0.28V) = -0.17V$$

Notice the negative value of the standard cell potential indicates the process is not spontaneous under standard conditions. Substitution of the Nernst equation terms for the nonstandard conditions requires calculating the reaction quotient Q

$$Q = \frac{[\mathrm{Co^{2+}}]}{[\mathrm{Fe^{2+}}]} = \frac{0.15M}{1.94M} = 0.077$$

them Q and n are substituted into Equation \red{Nernst at room temperature}

$$\begin{aligned} E_{\mathrm{cell}} &= E^\circ_{\mathrm{cell}} - \frac{0.0592\,\mathrm{V}}{n}\log Q \\ &= -0.17\,\mathrm{V} - \frac{0.0592\,\mathrm{V}}{2}\log 0.077 \\ &= -0.17\,\mathrm{V} + 0.033\,\mathrm{V} \\ &= -0.14\,\mathrm{V} \end{aligned}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Exercise 18.7.2

For the cell schematic below at room temperature, identify values for *n* and *Q*, and calculate the cell potential, E_{cell}.

$$\mathrm{Al(s)|Al^{3+}(aq,\ 0.15\ M)|Cu^{2+}(aq,\ 0.025\ M)|Cu(s)}$$

Answer

n = 6; *Q* = 1440; E_{cell} = +1.97 V, spontaneous.

A **concentration cell** is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode, varying only in the concentration of one redox species. The potential of a concentration cell, therefore, is determined only by the difference in concentration of the chosen redox species. The example problem below illustrates the use of the Nernst equation in calculations involving concentration cells.

Example 18.7.3: Concentration Cells

What is the cell potential of the concentration cell operating at room temperature described by

$$\mathrm{Zn(s)|Zn^{2+}(aq,\ 0.10\ M)|Zn^{2+}(aq,\ 0.50\ M)|Zn(s)}$$

Solution

From the information given:

$$\begin{array}{lll} \text{anode: } Zn(s) \longrightarrow Zn^{2+}(aq,\ 0.10\ M) + 2\,e^- & E^o_{Co^{2+}/Co} = -0.7618\,V \\ \text{cathode: } Zn^{2+}(aq,\ 0.50\ M) + 2\,e^- \longrightarrow Zn(s) & E^o_{Fe^{+}/Fe} = -0,7618\,V \\ \hline \text{cell: } \cancel{Zn(s)} + Zn^{2+}(aq,\ 0.50\ M) \longrightarrow Zn^{2+}(aq,\ 0.10\ M) + \cancel{Zn(s)} & E^o_{cell} = 0\,V \end{array}$$

Substituting into the Nernst equation (Equation 18.7.2),

$$E_{cell} = 0.000\,V - \frac{0.0592\,V}{2}\log\frac{0.10}{0.50} = +0.021\,V$$

The positive value for cell potential indicates the overall cell reaction (see above) is spontaneous. This spontaneous reaction is one in which the zinc ion concentration in the cathode falls (it is reduced to elemental zinc) while that in the anode rises (it is produced by oxidation of the zinc anode). A greater driving force for zinc reduction is present in the cathode, where the zinc(II) ion concentration is greater ($E_{cathode} > E_{anode}$).

? Exercise 18.7.1

The concentration cell above was allowed to operate until the cell reaction reached equilibrium at room temperature. What are the cell potential and the concentrations of zinc(II) in each half-cell for the cell now?

Answer

E_{cell} = 0.000 V; $[Zn^{2+}]_{cathode} = [Zn^{2+}]_{anode}$ = 0.30 *M*

This page titled 18.7: Potential, Free Energy, and Equilibrium is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.4: Potential, Free Energy, and Equilibrium** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.8: Batteries and Fuel Cells

Learning Objectives

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

- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

There are many technological products associated with the past two centuries of electrochemistry research, none more immediately obvious than the battery. A **battery** is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use a source of electrical power for specific applications. Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions (Figure 18.8.1):

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)}$$

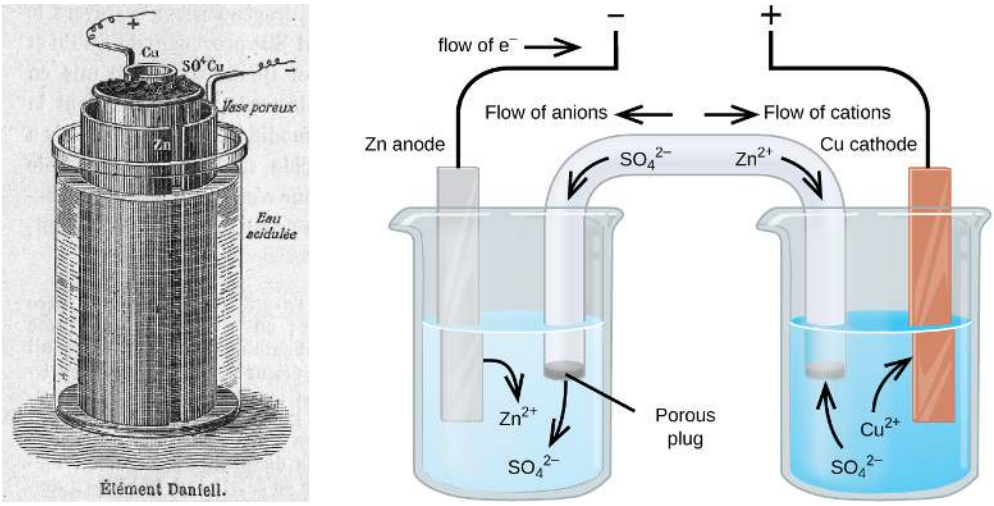


Figure 18.8.1: Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell's content and to serve as a salt bridge to the other half-cell.

Modern batteries exist in a multitude of forms to accommodate various applications, from tiny button batteries that provide the modest power needs of a wristwatch to the very large batteries used to supply backup energy to municipal power grids. Some batteries are designed for single-use applications and cannot be recharged (primary cells), while others are based on conveniently reversible cell reactions that allow recharging by an external power source (secondary cells). This section will provide a summary of the basic electrochemical aspects of several batteries familiar to most consumers, and will introduce a related electrochemical device called a *fuel cell* that can offer improved performance in certain applications.

Link to Learning

Visit this site to learn more about batteries.

Single-Use Batteries

A common primary battery is the dry cell, 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. A graphite rod is immersed in the electrolyte paste to complete the cell. The spontaneous cell reaction involves the oxidation of zinc:

$$\mathrm{Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^-} \qquad \textbf{(anode)}$$

and the reduction of manganese(IV)

$$2\,MnO_2\,(s) + 2\,NH_4Cl\,(aq) + 2\,e^- \longrightarrow Mn_2O_3\,(s) + 2\,NH_3\,(aq) + H_2O\,(l) + 2\,Cl^- \qquad \text{(cathode)}$$

which together yield the cell reaction:

$$2\,MnO_2\,(s) + 2\,NH_4Cl\,(aq) + Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + Mn_2O_3\,(s) + 2\,NH_3\,(aq) + H_2O\,(l) + 2\,Cl^- \qquad \text{(cell)}$$

The voltage (*cell potential*) of a dry cell is approximately 1.5 V. Dry cells are available in various sizes (e.g., D, C, AA, AAA). All sizes of dry cells comprise the same components, and so they exhibit the same voltage, but larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge. Like other galvanic cells, dry cells may be connected in series to yield batteries with greater voltage outputs, if needed.

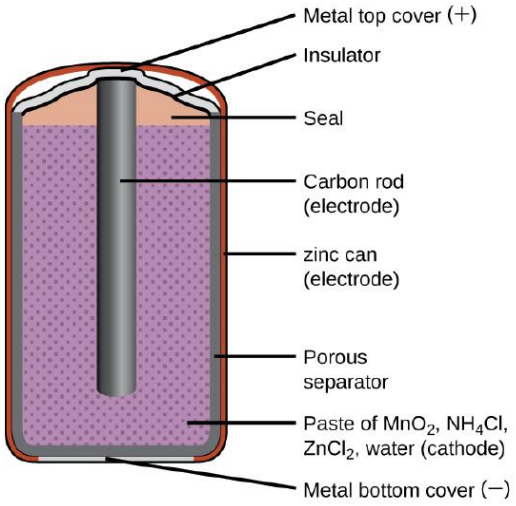


Figure **18.8.2**: A schematic diagram shows a typical dry cell.

Link to Learning

Visit this site to learn more about zinc-carbon batteries.

Alkaline batteries (Figure **18.8.3**) were developed in the 1950s to improve on the performance of the dry cell, and they were designed around the same redox couples. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

anode:	$Zn\,(s) + 2\,OH^-\,(aq) \longrightarrow ZnO\,(s) + H_2O\,(l) + 2\,e^-$
cathode:	$2\,MnO_2\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow Mn_2O_3\,(s) + 2\,OH^-\,(aq)$
cell:	$Zn\,(s) + 2\,MnO_2\,(s) \longrightarrow ZnO\,(s) + Mn_2O_3\,(s) \qquad E_{cell} = +1.43\,V$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so they should be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

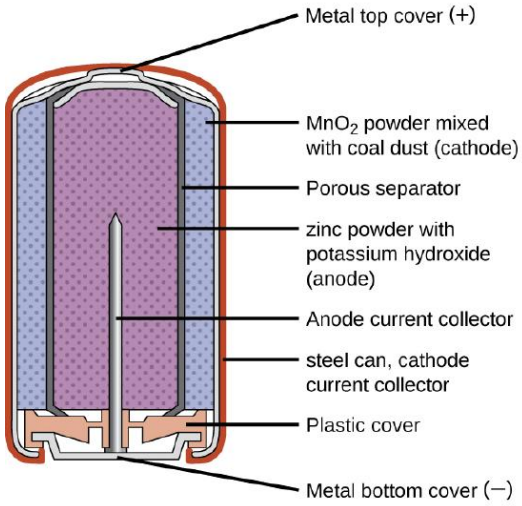


Figure 18.8.3: Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.

Link to Learning

Visit this site to learn more about alkaline batteries.

Rechargeable (Secondary) Batteries

Nickel-cadmium, or NiCd, batteries (Figure 18.8.4) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{array}{lll} \text{anode:} & \mathrm{Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-} & \\ \text{cathode:} & \mathrm{NiO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow Ni(OH)_2(s) + 2\,OH^-(aq)} & \\ \hline \text{cell:} & \mathrm{Cd(s) + NiO_2(s) + 2\,H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)} & E_{\text{cell}} \approx +1.2\,\text{V} \end{array}$$

When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be ruptured or incinerated, and they should be disposed of in accordance with relevant toxic waste guidelines.

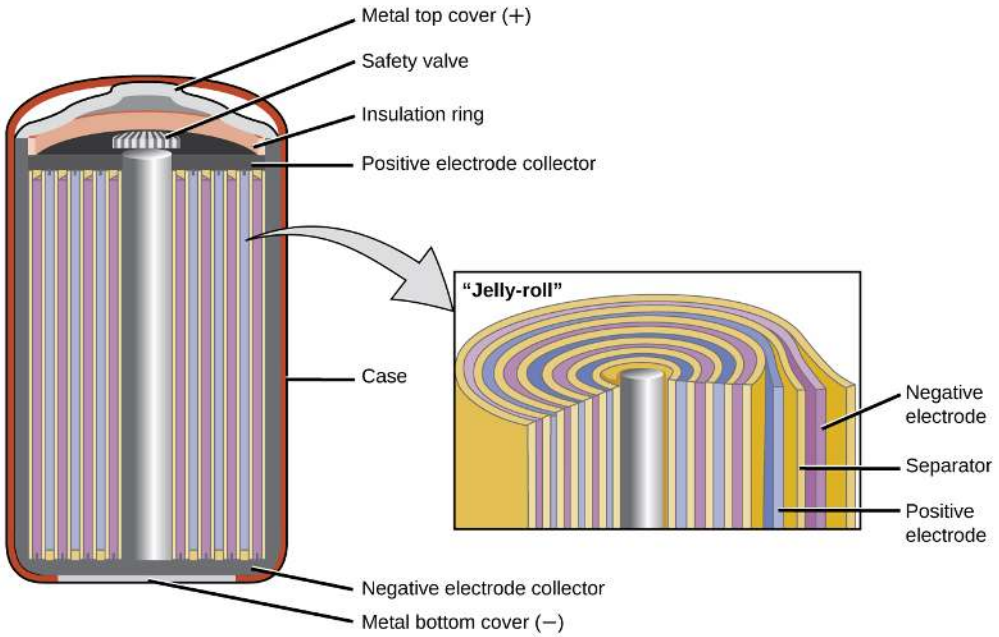


Figure 18.8.4: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Link to Learning

Visit this site for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries (Figure 18.8.5) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{ll} \textbf{anode:} & \mathrm{LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + x\ Li^+ + x\ e^-} \\ \textbf{cathode:} & \mathrm{x\ Li^+ + x\ e^- + x\ C_6 \longrightarrow x\ LiC_6} \\ \hline \textbf{cell:} & \mathrm{LiCoO_2 + x\ C_6 \longrightarrow Li_{1-x}CoO_2 + x\ LiC_6} \qquad E_{\text{cell}} \approx +3.7\,\text{V} \end{array}$$

The variable stoichiometry of the cell reaction leads to variation in cell voltages, but for typical conditions, x is usually no more than 0.5 and the cell voltage is approximately 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

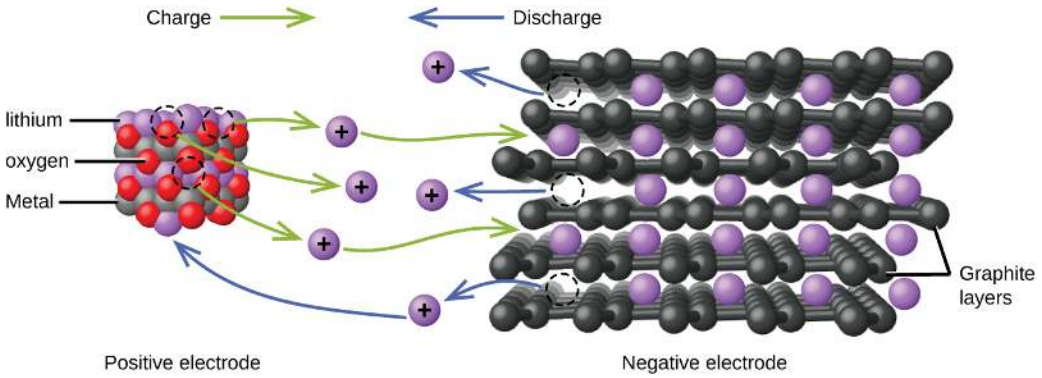


Figure 18.8.5: In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.

Link to Learning

Visit this site for more information about lithium ion batteries.

The lead acid battery (Figure 18.8.6) is the type of secondary battery commonly used in automobiles. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{array}{ll} \textbf{anode:} & \mathrm{Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^-} \\ \textbf{cathode:} & \mathrm{PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)} \\ \hline \textbf{cell:} & \mathrm{Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)} \qquad E_{\text{cell}} \approx +2\,\text{V} \end{array}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, $H_2SO_4(aq)$, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

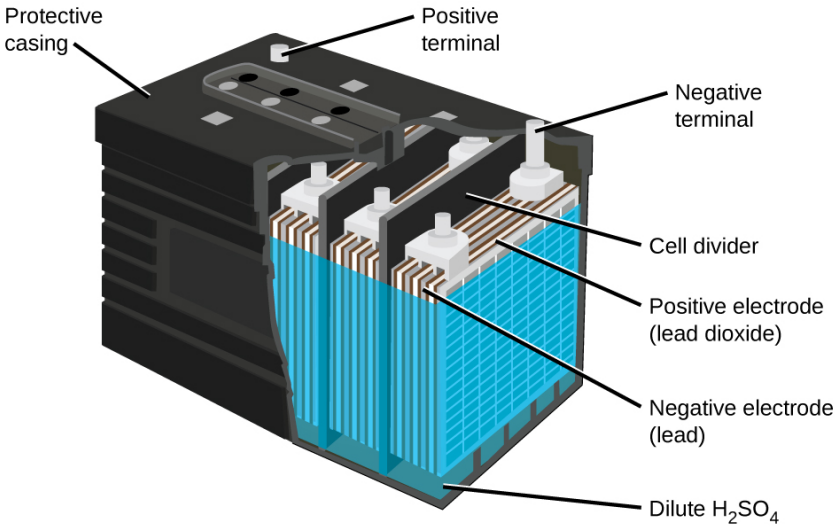


Figure 18.8.6: The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

Link to Learning

Visit this site for more information about lead acid batteries.

Fuel Cells

A fuel cell is a galvanic cell that uses traditional combustive fuels, most often hydrogen or methane, that are continuously fed into the cell along with an oxidant. (An alternative, but not very popular, name for a fuel cell is a *flow battery*.) Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted, but via a catalyzed electrochemical that is significantly more efficient. For example, a typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions:

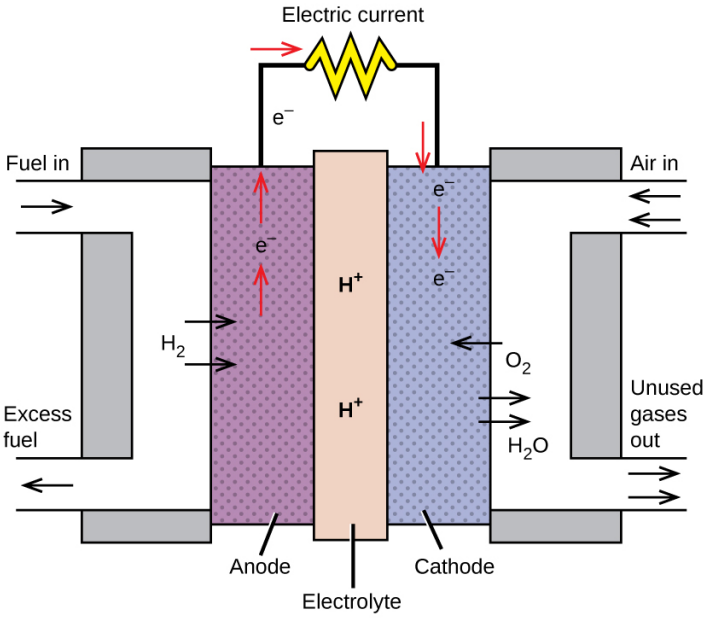


Figure 18.8.7: In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.

$$\begin{array}{ll} \textbf{anode:} & 2\,H_2\,(g) \longrightarrow 4\,H^+\,(aq) + 4\,e^- \\ \textbf{cathode:} & O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(g) \\ \hline \textbf{cell:} & 2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g) \qquad E_{cell} \approx +1.2\,V \end{array}$$

These types of fuel cells generally produce voltages of approximately 1.2 V. Compared to an internal combustion engine, the energy efficiency of a fuel cell using the same redox reaction is typically more than double (~20%–25% for an engine versus ~50%–75% for a fuel cell). Hydrogen fuel cells are commonly used on extended space missions, and prototypes for personal vehicles have been developed, though the technology remains relatively immature.

Link to Learning

Check out this link to learn more about fuel cells.

This page titled 18.8: Batteries and Fuel Cells is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.5: Batteries and Fuel Cells** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.9: Corrosion

Learning Objectives

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

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals by a naturally occurring electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion remediation in the United States is significant, with estimates in excess of half a trillion dollars a year.

Chemistry in Everyday Life: Statue of Liberty: Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color (Figure **18.9.1**). When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

$$2\,Cu\,(s) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow Cu_2\,O\,(s) \qquad \textbf{(red)}$$

$$2\,Cu_2O\,(s) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow 2\,CuO\,(s) \qquad \textbf{(black)}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, atmospheric sulfur trioxide, carbon dioxide, and water all reacted with the **CuO**:

$$2\,CuO\,(s) + CO_2\,(g) + H_2O\,(l) \longrightarrow Cu_2CO_3(OH)_2\,(s) \qquad \textbf{(green)}$$

$$3\,CuO\,(s) + 2\,CO_2\,(g) + H_2O\,(l) \longrightarrow Cu_2(CO_3)_2(OH)_2\,(s) \qquad \textbf{(blue)}$$

$$4\,CuO\,(s) + SO_3\,(g) + 3\,H_2O\,(l) \longrightarrow Cu_4SO_4(OH)_6\,(s) \qquad \textbf{(green)}$$

These three compounds are responsible for the characteristic blue-green patina seen on the Statue of Liberty (and other outdoor copper structures). Fortunately, formation of patina creates a protective layer on the copper surface, preventing further corrosion of the underlying copper. The formation of the protective layer is called *passivation*, a phenomenon discussed further in another chapter of this text.



(a) (b)

Figure 18.9.1: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. Rust formation involves the creation of a galvanic cell at an iron surface, as illustrated in Figure 18.9.1. The relevant redox reactions are described by the following equations:

anode:	$\mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-}$	$E^\circ_{\mathrm{Fe^{2+}\,/\,Fe}} = -0.44\,\mathrm{V}$
cathode:	$\mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O(l)}$	$E^\circ_{\mathrm{O_2\,/O^{2-}}} = +1.23\,\mathrm{V}$
overall:	$2\,\mathrm{Fe(s)} + \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} \longrightarrow 2\,\mathrm{Fe^{2+}(aq)} + 2\,\mathrm{H_2O(l)}$	$E^\circ_{\mathrm{cell}} = +1.67\,\mathrm{V}$

Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:

$$4\,\mathrm{Fe^{2+}(aq)} + \mathrm{O_2(g)} + (4+2x)\ \mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{Fe_2O_3}\cdot x\ \mathrm{H_2O(s)} + 8\,\mathrm{H^+(aq)}$$

The stoichiometry of the hydrate varies, as indicated by the use of x in the compound formula. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

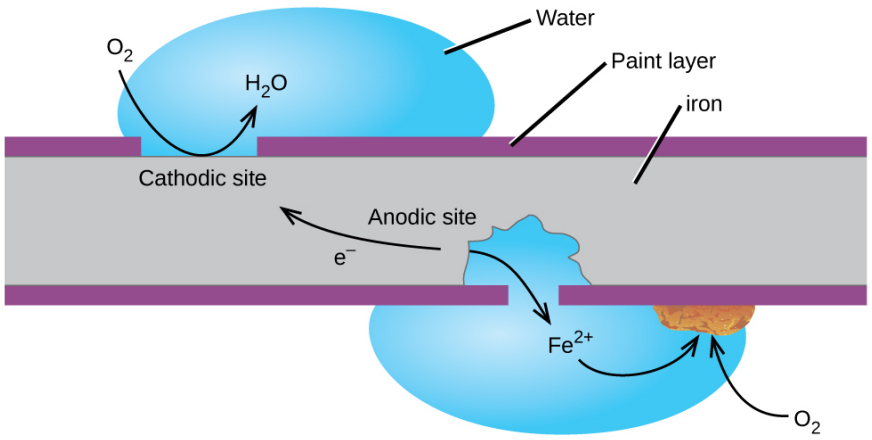


Figure 18.9.2: Corrosion can occur when a painted iron or steel surface is exposed to the environment by a scratch through the paint. A galvanic cell results that may be approximated by the simplified cell schematic Fe(s) | $Fe^{2+}(aq)$ ||$O_2(aq)$, $H_2O(l)$ | Fe(s).

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is an alloy of iron containing a small amount of chromium. The chromium tends to collect near the surface, where it corrodes and forms a passivating an oxide layer that protects the iron.

Iron and other metals may also be protected from corrosion by **galvanization**, a process in which the metal to be protected is coated with a layer of a more readily oxidized metal, usually zinc. When the zinc layer is intact, it prevents air from contacting the underlying iron and thus prevents corrosion. If the zinc layer is breached by either corrosion or mechanical abrasion, the iron may still be protected from corrosion by a *cathodic protection* process, which is described in the next paragraph.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (Figure **18.9.3**). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode for the reduction of oxygen in air, and so it simply serves to conduct (not react with) the electrons being transferred. When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

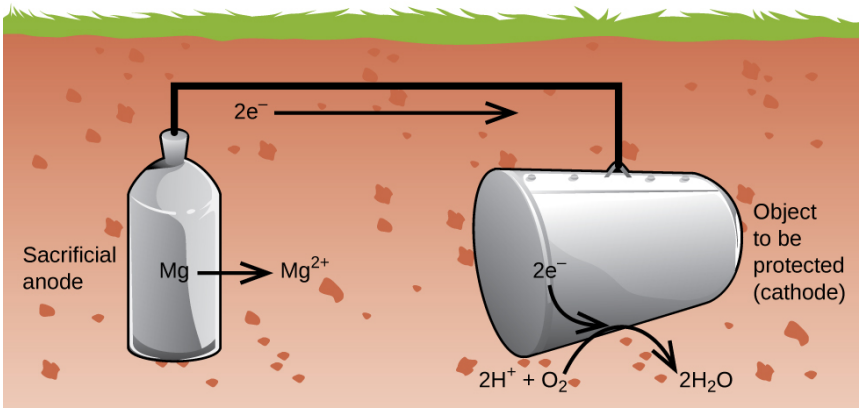


Figure **18.9.3**: Cathodic protection is a useful approach to electrochemically preventing corrosion of underground storage tanks.

This page titled 18.9: Corrosion is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.6: Corrosion** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.10: Electrolysis

Learning Objectives

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

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrochemical cells in which spontaneous redox reactions take place (*galvanic cells*) have been the topic of discussion so far in this chapter. In these cells, *electrical work is done by a redox system on its surroundings* as electrons produced by the redox reaction are transferred through an external circuit. This final section of the chapter will address an alternative scenario in which *an external circuit does work on a redox system* by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction, a process known as **electrolysis**. A familiar example of electrolysis is recharging a battery, which involves use of an external power source to drive the spontaneous (discharge) cell reaction in the reverse direction, restoring to some extent the composition of the half-cells and the voltage of the battery. Perhaps less familiar is the use of electrolysis in the refinement of metallic ores, the manufacture of commodity chemicals, and the *electroplating* of metallic coatings on various products (e.g., jewelry, utensils, auto parts). To illustrate the essential concepts of electrolysis, a few specific processes will be considered.

The Electrolysis of Molten Sodium Chloride

Metallic sodium, Na, and chlorine gas, Cl_2, are used in numerous applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl(*l*). The industrial process typically uses a *Downs cell* similar to the simplified illustration shown in Figure **18.10.1**. The reactions associated with this process are:

Extra close brace or missing open brace

The cell potential for the above process is negative, indicating the reaction as written (decomposition of liquid NaCl) is not spontaneous. To force this reaction, *a positive potential of magnitude greater than the negative cell potential* must be applied to the cell.

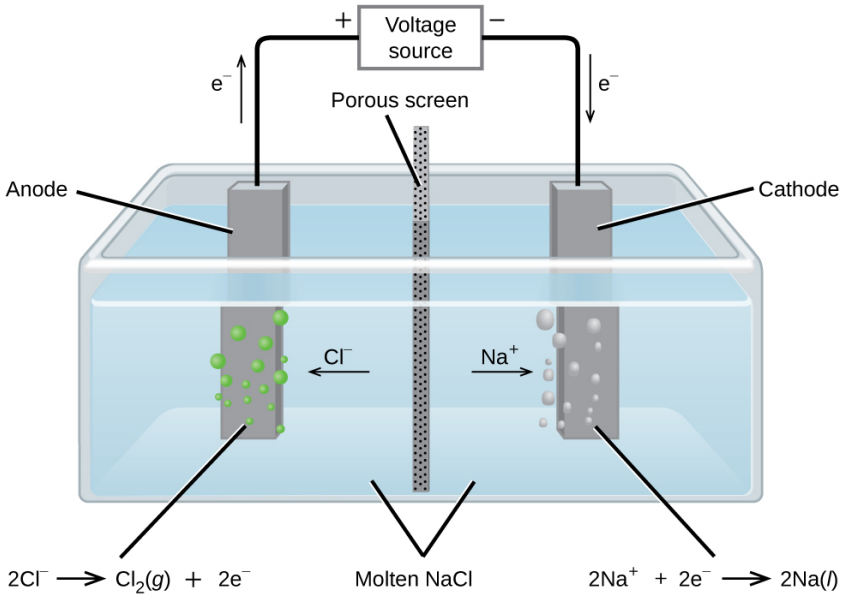


Figure **18.10.1**: Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the *Downs process* for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.

The Electrolysis of Water

Water may be electrolytically decomposed in a cell similar to the one illustrated in Figure 18.10.2. To improve electrical conductivity without introducing a different redox species, the hydrogen ion concentration of the water is typically increased by addition of a strong acid. The redox processes associated with this cell are

Extra close brace or missing open brace

Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by imposing a cell voltage greater than +1.229 V. Keep in mind that *standard* electrode potentials are used to inform thermodynamic predictions here, though the cell is *not* operating under standard state conditions. Therefore, at best, calculated cell potentials should be considered ballpark estimates.

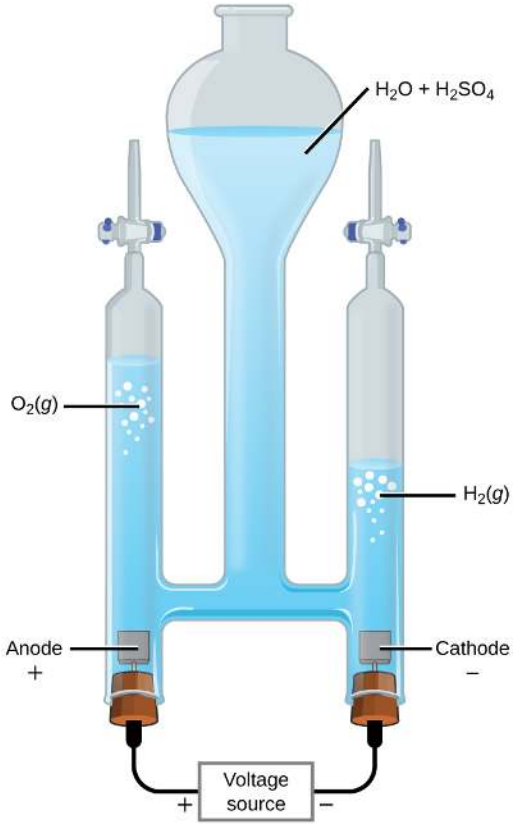


Figure 18.10.2: The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.

The Electrolysis of Aqueous Sodium Chloride

When aqueous solutions of ionic compounds are electrolyzed, the anode and cathode half-reactions may involve the electrolysis of either water species (H_2O, H^+, OH^-) or solute species (the cations and anions of the compound). As an example, the electrolysis of aqueous sodium chloride could involve either of these two anode reactions:

$$2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- \quad E^\circ_{anode} = +1.35827\,V \tag{i}$$

or

$$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad E^\circ_{anode} = +1.229\,V \tag{ii}$$

The standard electrode (*reduction*) potentials of these two half-reactions indicate water may be *oxidized* at a less negative/more positive potential (–1.229 V) than chloride ion (–1.358 V). Thermodynamics thus predicts that water would be more readily oxidized, though in practice it is observed that both water and chloride ion are oxidized under typical conditions, producing a mixture of oxygen and chlorine gas.

Turning attention to the cathode, the possibilities for reduction are:

$$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad E^\circ_{anode} = 0\,V \tag{iii}$$

or

$$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 4\,OH^-(aq) \quad E^\circ_{anode} = -0.8277\,V \tag{iv}$$

or

$$Na^+(aq) + e^- \longrightarrow Na(s) \quad E^\circ_{anode} = -2.71\,V \tag{v}$$

Comparison of these *standard* half-reaction potentials suggests the reduction of hydrogen ion is thermodynamically favored. However, in a neutral aqueous sodium chloride solution, the concentration of hydrogen ion is far below the standard state value of 1 *M* (approximately 10^{-7} *M*), and so the observed cathode reaction is actually reduction of water. The net cell reaction in this case is then

$$2\,H_2O(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2\,OH^-(aq) \quad E^\circ_{cell} = -2.186\,V$$

This electrolysis reaction is part of the *chlor-alkali process* used by industry to produce chlorine and sodium hydroxide (lye).

Chemistry in Everyday Life: Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. The silver plating of eating utensils is used here to illustrate the process. (Figure **18.10.3**).

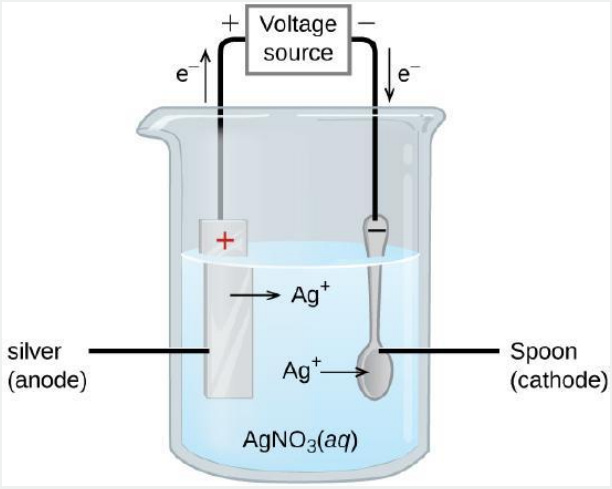


Figure **18.10.3**: This schematic shows an electrolytic cell for silver plating eating utensils.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. Applying a sufficient potential results in the oxidation of the silver anode

$$Ag(s) \longrightarrow Ag^+(aq) + e^- \qquad \text{(anode)}$$

and reduction of silver ion at the (spoon) cathode:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad \text{(cathode)}$$

The net result is the transfer of silver metal from the anode to the cathode. Several experimental factors must be carefully controlled to obtain high-quality silver coatings, including the exact composition of the electrolyte solution, the cell voltage applied, and the rate of the electrolysis reaction (electrical current).

Quantitative Aspects of Electrolysis

Electrical current is defined as the rate of flow for any charged species. Most relevant to this discussion is the flow of electrons. Current is measured in a composite unit called an ampere, defined as one coulomb per second (A = 1 C/s). The charge transferred, *Q*, by passage of a constant current, *I*, over a specified time interval, *t*, is then given by the simple mathematical product

$$Q = It$$

When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved. For example, the generic reduction process

$$\mathrm{M}^{n+}(\mathrm{aq}) + \mathrm{n\,e}^- \longrightarrow \mathrm{M}(\mathrm{s})$$

involves the transfer of n mole of electrons. The total charge transferred is, therefore,

$$Q = nF$$

where F is Faraday's constant, the charge in coulombs for one mole of electrons. If the reaction takes place in an electrochemical cell, the current flow is conveniently measured, and it may be used to assist in stoichiometric calculations related to the cell reaction.

Example 18.10.1: 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 exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23C}{s} \times 1hr \times \frac{60min}{hr} \times \frac{60s}{\text{min}}}{96,485C/mole^-} = \frac{36,830C}{96,485C/mole^-} = 0.3817mole^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\mathrm{Ag}^+(\mathrm{aq}) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(\mathrm{s}) \qquad \text{(cathode)}$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass } Ag = 0.3817\,\text{mol e}^- \times \frac{1\,\text{mol Ag}}{1\,\text{mol e}^-} \times \frac{107.9\,\text{g Ag}}{1\,\text{mol Ag}} = 41.19\,\text{g Ag}$$

Exercise 18.10.1

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

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$$

0.0777 mol Al = 2.10 g Al.

Example 18.10.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46

A? The density of chromium (metal) is 7.19 g/cm^3.

Solution

First, compute the volume of chromium that must be produced (equal to the product of surface area and thickness):

$$\text{volume } = \left(0.010mm \times \frac{1cm}{10mm}\right) \times \left(3.3m^2 \times \left(\frac{10,000cm^2}{1m^2}\right)\right) = 33cm^3$$

Use the computed volume and the provided density to calculate the molar amount of chromium required:

$$\text{mass } = \text{ volume } \times \text{ density } = 33cm^3 \times \frac{7.19g}{cm^3} = 237gCr$$

$$molCr = 237gCr \times \frac{1molCr}{52.00gCr} = 4.56molCr$$

The stoichiometry of the chromium(III) reduction process requires three moles of electrons for each mole of chromium(0) produced, and so the total charge required is:

$$Q = 4.56molCr \times \frac{3mole^-}{1molCr} \times \frac{96485C}{mole^-} = 1.32 \times 10^6C$$

Finally, if this charge is passed at a rate of 33.46 C/s, the required time is:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6C}{33.46C/s} = 3.95 \times 10^4s = 11.0hr$$

? Exercise 18.10.2

What mass of zinc is required to galvanize the top of a 3.00 m 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

11.8 kg Zn requires 382 hours.

This page titled 18.10: Electrolysis is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **17.7: Electrolysis** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

18.11: Key Terms

active electrode | electrode that participates as a reactant or product in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

alkaline battery | primary battery similar to a *dry cell* that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an improved replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

anode | electrode in an electrochemical cell at which oxidation occurs

battery | single or series of galvanic cells designed for use as a source of electrical power

cathode | electrode in an electrochemical cell at which reduction occurs

cathodic protection | approach to preventing corrosion of a metal object by connecting it to a *sacrificial anode* composed of a more readily oxidized metal

cell notation (schematic) | symbolic representation of the components and reactions in an electrochemical cell

cell potential (E_{cell}) | difference in potential of the cathode and anode half-cells

concentration cell | galvanic cell comprising half-cells of identical composition but for the concentration of one redox reactant or product

corrosion | degradation of metal via a natural electrochemical process

dry cell | primary battery, also called a zinc-carbon battery, based on the spontaneous oxidation of zinc by manganese(IV)

electrode potential (E_X) | the potential of a cell in which the half-cell of interest acts as a cathode when connected to the standard hydrogen electrode

electrolysis | process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell | electrochemical cell in which an external source of electrical power is used to drive an otherwise nonspontaneous process

Faraday's constant (F) | charge on 1 mol of electrons; F = 96,485 C/mol e^-

fuel cell | devices similar to galvanic cells that require a continuous feed of redox reactants; also called a *flow battery*

galvanic (voltaic) cell | electrochemical cell in which a spontaneous redox reaction takes place; also called a *voltaic cell*

galvanization | method of protecting iron or similar metals from corrosion by coating with a thin layer of more easily oxidized zinc.

half cell | component of a cell that contains the redox conjugate pair ("couple") of a single reactant

inert electrode | electrode that conducts electrons to and from the reactants in a half-cell but that is not itself oxidized or reduced

lead acid battery | rechargeable battery commonly used in automobiles; it typically comprises six galvanic cells based on Pb half-reactions in acidic solution

lithium ion battery | widely used rechargeable battery commonly used in portable electronic devices, based on lithium ion transfer between the anode and cathode

Nernst equation | relating the potential of a redox system to its composition

nickel-cadmium battery | rechargeable battery based on Ni/Cd half-cells with applications similar to those of lithium ion batteries

primary cell | nonrechargeable battery, suitable for single use only

sacrificial anode | electrode constructed from an easily oxidized metal, often magnesium or zinc, used to prevent corrosion of metal objects via cathodic protection

salt bridge | tube filled with inert electrolyte solution

secondary cell | battery designed to allow recharging

standard cell potential | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 M for solutes), usually at 298.15 K

standard electrode potential () | electrode potential measured under standard conditions (1 bar or 1 atm for gases; 1 M for solutes) usually at 298.15 K

standard hydrogen electrode (SHE) | half-cell based on hydrogen ion production, assigned a potential of exactly 0 V under standard state conditions, used as the universal reference for measuring electrode potential

18.11: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **17.8: Key Terms** is licensed CC BY 4.0.

18.12: Key Equations

$$\Delta G = -nFE_{\text{cell}}$$

$$Q = I\,t = n\,F$$

18.12: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **17.9: Key Equations** is licensed CC BY 4.0.

CHAPTER OVERVIEW

19: Nuclear Chemistry

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the **electrons** around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions. This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

19.1: Introduction
19.2: Exercises
19.3: Nuclear Structure and Stability
19.4: Nuclear Equations
19.5: Radioactive Decay
19.6: Transmutation and Nuclear Energy
19.7: Uses of Radioisotopes
19.8: Biological Effects of Radiation
19.9: Key Terms
19.10: Key Equations
19.11: Summary

This page titled 19: Nuclear Chemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

19.1: Introduction

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the electrons around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions.

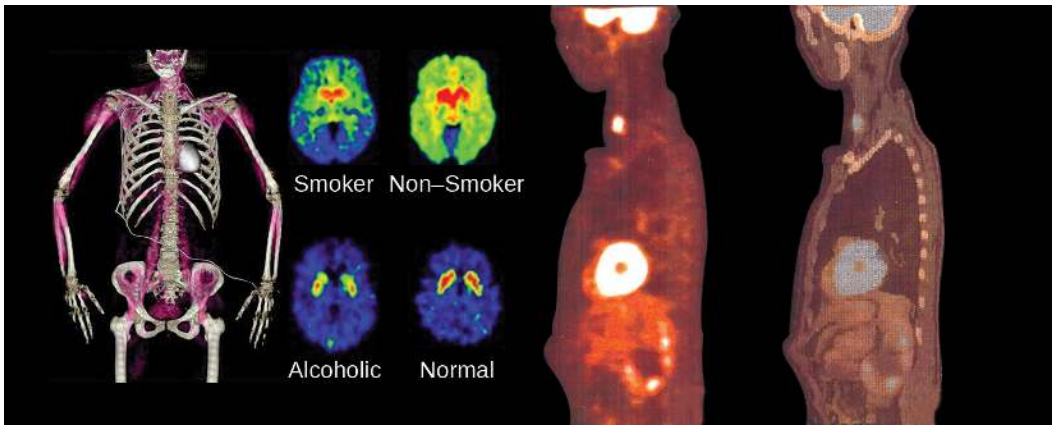


Figure **19.1.1**: Nuclear chemistry provides the basis for many useful diagnostic and therapeutic methods in medicine, such as these positron emission tomography (PET) scans. The PET/computed tomography scan on the left shows muscle activity. The brain scans in the center show chemical differences in dopamine signaling in the brains of addicts and nonaddicts. The images on the right show an oncological application of PET scans to identify lymph node metastasis.

This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

19.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **21.0: Introduction** is licensed CC BY 4.0.

19.2: Exercises

1. Write the following isotopes in hyphenated form (e.g., “carbon-14”)

(a) $^{24}_{11}\mathrm{Na}$
(b) $^{29}_{13}\mathrm{Al}$
(c) $^{73}_{36}\mathrm{Kr}$
(d) $^{194}_{77}\mathrm{Ir}$

2. Write the following isotopes in nuclide notation (e.g.,

a. oxygen-14
b. copper-70
c. tantalum-175
d. francium-217

3. For the following isotopes that have missing information, fill in the missing information to complete the notation

(a) $^{34}_{14}\mathrm{X}$
(b) $^{36}_{X}\mathrm{P}$
(c) $^{57}_{X}\mathrm{Mn}$
(d) $^{121}_{56}\mathrm{X}$

4. For each of the isotopes in Exercise 21.1, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

5. Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

a. 25 protons, 20 neutrons, 24 electrons
b. 45 protons, 24 neutrons, 43 electrons
c. 53 protons, 89 neutrons, 54 electrons
d. 97 protons, 146 neutrons, 97 electrons

6. Calculate the density of the nucleus in g/mL, assuming that it has the typical nuclear diameter of 1 10^{-13} cm and is spherical in shape. 7. What are the two principal differences between nuclear reactions and ordinary chemical changes?

8. The mass of the atom is 22.9898 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

9. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

a. chlorine-37
b. calcium-40
c. $^{204}\mathrm{Bi}$
d. $^{56}\mathrm{Fe}$
e. $^{206}\mathrm{Pb}$
f. $^{211}\mathrm{Pb}$
g. $^{222}\mathrm{Rn}$
h. carbon-14

10. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

a. argon-40
b. oxygen-16
c. $^{122}\mathrm{Ba}$
d. $^{58}\mathrm{Ni}$
e. $^{205}\mathrm{Tl}$

f. ^{210}Tl
g. ^{226}Ra
h. magnesium-24

11. Write a brief description or definition of each of the following:

a. nucleon
b. α particle
c. β particle
d. positron
e. γ ray
f. nuclide
g. mass number
h. atomic number

12. Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

13. Complete each of the following equations by adding the missing species:

(a) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow \text{?} + {}^{1}_{0}\text{n}$
(b) $^{239}_{94}\text{Pu} + \text{?} \rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
(c) $^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow \text{?} + {}^{1}_{1}\text{H}$
(d) $^{235}_{92}\text{U} \rightarrow \text{?} + {}^{135}_{55}\text{Cs} + 4{}^{1}_{0}\text{n}$

14. Complete each of the following equations:

(a) $^{7}_{3}\text{Li} + \text{?} \rightarrow 2{}^{4}_{2}\text{He}$
(b) $^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + \text{?}$
(c) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow \text{?} + {}^{1}_{0}\text{n}$
(d) $^{250}_{96}\text{Cm} \rightarrow \text{?} + {}^{98}_{38}\text{Sr} + 4{}^{1}_{0}\text{n}$

15. Write a balanced equation for each of the following nuclear reactions:

a. the production of ^{17}O from ^{14}N by α particle bombardment
b. the production of ^{14}C from ^{14}N by neutron bombardment
c. the production of ^{233}Th from ^{232}Th by neutron bombardment
d. the production of ^{239}U from ^{238}U by bombardment

16. Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as ^{99}Tc*. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

17. The mass of the atom is 18.99840 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

18. For the reaction if 100.0 g of carbon reacts, what volume of nitrogen gas (N_2) is produced at 273K and 1 atm?

19. What are the types of radiation emitted by the nuclei of radioactive elements?

20. What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

a. an α particle is emitted
b. a β particle is emitted
c. γ radiation is emitted
d. a positron is emitted
e. an electron is captured

21. What is the change in the nucleus that results from the following decay scenarios?

a. emission of a β particle
b. emission of a β^+ particle
c. capture of an electron

22. Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

23. Why is electron capture accompanied by the emission of an X-ray?

24. Explain, in terms of Figure 21.2, how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

25. Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

a. chromium-53
b. manganese-51
c. iron-59

26. The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.

(a) $^{34}_{15}\mathrm{P}$
(b) $^{239}_{92}U$
(c) $^{38}_{20}\mathrm{Ca}$
(d) $^{3}_{1}\mathrm{H}$
(e) $^{245}_{94}\mathrm{Pu}$

27. The following nuclei do not lie in the band of stability. How would they be expected to decay?

(a) $^{28}_{15}\mathrm{P}$
(b) $^{235}_{92}\mathrm{U}$
(c) $^{37}_{20}\mathrm{Ca}$
(d) $^{9}_{3}\mathrm{Li}$
(e) $^{245}_{96}\mathrm{Cm}$

28. Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

(a) $^{6}_{2}\mathrm{He}$
(b) $^{60}_{30}\mathrm{Zn}$
(c) $^{235}_{91}\ \mathrm{Pa}$
(d) $^{241}_{94}\ \mathrm{Np}$
(e) $^{18}\ \mathrm{F}$
(f) $^{129}\mathrm{Ba}$
(g) $^{237}\mathrm{Pu}$

29. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α particles, in that order.

30. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

31. Define the term half-life and illustrate it with an example.

32. A 1.00 10^{-6}-g sample of nobelium, has a half-life of 55 seconds after it is formed. What is the percentage of remaining at the following times?

a. 5.0 min after it forms
b. 1.0 h after it forms

33. ^{239}Pu is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the ^{239}Pu present today will be present in 1000 y?

34. The isotope ^{208}Tl undergoes β decay with a half-life of 3.1 min.

a. What isotope is produced by the decay?
b. How long will it take for 99.0% of a sample of pure ^{208}Tl to decay?
c. What percentage of a sample of pure ^{208}Tl remains un-decayed after 1.0 h?

35. If 1.000 g of produces 0.0001 mL of the gas at STP (standard temperature and pressure) in 24 h, what is the half-life of ^{226}Ra in years?

36. The isotope is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.

37. Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of

38. What is the age of mummified primate skin that contains 8.25% of the original quantity of ^{14}C?

39. A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.

a. Calculate the age of the rock if the half-life of the decay of rubidium by β emission is $4.7\ 10^{10}$ y.
b. If some was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.

40. A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of and 2.52 mg of Calculate the age of the ore. The half-life of is $4.5\ 10^{9}$ yr.

41. Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this ^{239}Pu was the capture of neutrons by ^{238}U nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed $4.7\ 10^{9}$ years ago?

42. A atom (mass = 7.0169 amu) decays into a atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?

43. A atom (mass = 8.0246 amu) decays into a atom (mass = 8.0053 amu) by loss of a β^+ particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?

44. Isotopes such as ^{26}Al (half-life: $7.2\ 10^{5}$ years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

a. ^{26}Al decays by β^+ emission or electron capture. Write the equations for these two nuclear transformations.
b. The earth was formed about $4.7\ 10^{9}$ (4.7 billion) years ago. How old was the earth when 99.999999% of the ^{26}Al originally present had decayed?

45. Write a balanced equation for each of the following nuclear reactions:

a. bismuth-212 decays into polonium-212
b. beryllium-8 and a positron are produced by the decay of an unstable nucleus
c. neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239
d. strontium-90 decays into yttrium-90

46. Write a balanced equation for each of the following nuclear reactions:

a. mercury-180 decays into platinum-176
b. zirconium-90 and an electron are produced by the decay of an unstable nucleus
c. thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay
d. neon-19 decays into fluorine-19

47. Write the balanced nuclear equation for the production of the following transuranium elements:

a. berkelium-244, made by the reaction of Am-241 and He-4
b. fermium-254, made by the reaction of Pu-239 with a large number of neutrons
c. lawrencium-257, made by the reaction of Cf-250 and B-11
d. dubnium-260, made by the reaction of Cf-249 and N-15

48. How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

49. Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

50.Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

51. Describe the components of a nuclear reactor.

52. In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

53. Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

54. The mass of a hydrogen atom is 1.007825 amu; that of a tritium atom is 3.01605 amu; and that of an α particle is 4.00150 amu. How much energy in kilojoules per mole of produced is released by the following fusion reaction:

55. How can a radioactive nuclide be used to show that the equilibrium is a dynamic equilibrium?

56. Technetium-99m has a half-life of 6.01 hours. If a patient injected with technetium-99m is safe to leave the hospital once 75% of the dose has decayed, when is the patient allowed to leave?

57. Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-133 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β^- emission.

a. Write an equation for the decay.
b. How long will it take for 95.0% of a dose of I-131 to decay?

58. If a hospital were storing radioisotopes, what is the minimum containment needed to protect against:

a. cobalt-60 (a strong γ emitter used for irradiation)
b. molybdenum-99 (a beta emitter used to produce technetium-99 for imaging)

59. Based on what is known about Radon-222's primary decay method, why is inhalation so dangerous?

60. Given specimens uranium-232 ($t_{1/2}$ = 68.9 y) and uranium-233 ($t_{1/2}$ = 159,200 y) of equal mass, which one would have greater activity and why?

61. A scientist is studying a 2.234 g sample of thorium-229 ($t_{1/2}$ = 7340 y) in a laboratory.

a. What is its activity in Bq?
b. What is its activity in Ci?

62. Given specimens neon-24 ($t_{1/2}$ = 3.38 min) and bismuth-211 ($t_{1/2}$ = 2.14 min) of equal mass, which one would have greater activity and why?

This page titled 19.2: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **21.10: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

19.3: Nuclear Structure and Stability

Learning Objectives

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

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of $^{1}_{1}\mathrm{H}$.

Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation $^{Z}_{A}\mathrm{X}$, where X is the symbol for the element, A is the mass number, and Z is the atomic number (for example, $^{14}_{6}\mathrm{C}$). Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_{6}\mathrm{C}$ is called "carbon-14."

Protons and neutrons, collectively called **nucleons**, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^{6} meters, 30,000 times larger). Example 19.3.1 demonstrates just how great nuclear densities can be in the natural world.

Example 19.3.1: Density of a Neutron Star

Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star's outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass = $M_{\odot}$ = mass of the sun = $1.99 \times 10^{30}\ kg$) and a diameter of 26 km.

a. What is the density of this neutron star?
b. How does this neutron star's density compare to the density of a uranium nucleus, which has a diameter of about 15 fm (1 fm = 10^{-15} m)?

Solution

We can treat both the neutron star and the U-235 nucleus as spheres. Then the density for both is given by:

$$d = \frac{m}{V} \quad \text{with} \quad V = \frac{4}{3}\pi r^3$$

a. The radius of the neutron star is so the density of the neutron star is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{2.4\left(1.99 \times 10^{30}\,\mathrm{kg}\right)}{\frac{4}{3}\pi\left(1.3 \times 10^{4} m\right)^3} = 5.2 \times 10^{17}\,\mathrm{kg/m^3}$$

b. The radius of the U-235 nucleus is so the density of the U-235 nucleus is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{235\,\mathrm{amu}\left(\frac{1.66 \times 10^{-27}\,\mathrm{kg}}{1\,\mathrm{amu}}\right)}{\frac{4}{3}\pi\left(7.5 \times 10^{-15}\,\mathrm{m}\right)^3} = 2.2 \times 10^{17}\,\mathrm{kg/m^3}$$

These values are fairly similar (same order of magnitude), but the neutron star is more than twice as dense as the U-235 nucleus.

? Exercise 19.3.1

Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of $1.75\ \text{fm}$ ($1\ \text{fm} = 1 \times 10^{-15}\ \text{m}$).

Answer

The density of the neutron star is $3.4 \times 10^{18}\ \text{kg/m}^3$. The density of a hydrogen nucleus is Extra close brace or missing open brace. The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the strong nuclear force. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

Link to Learning

Visit this website for more information about the four fundamental forces.

Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\underbrace{(2 \times 1.0073\ \text{amu})}_{\text{protons}} + \underbrace{(2 \times 1.0087\ \text{amu})}_{\text{neutrons}} + \underbrace{(2 \times 0.00055\ \text{amu})}_{\text{electrons}} = 4.0331\ \text{amu}$$

However, mass spectrometric measurements reveal that the mass of an atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the mass defect of the atom. In the case of helium, the **mass defect** indicates a “loss” in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The **nuclear binding energy** is the energy produced when the atoms’ nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the **mass-energy equivalence equation** as stated by Albert Einstein:

$$E = mc^2 \tag{19.3.1}$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its mass defect, as demonstrated in Example **19.3.2**. A variety of units are commonly used for nuclear binding energies, including electron volts (eV), with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making 1 eV = 1.602 10^{-19} J.

Example 19.3.2: Calculation of Nuclear Binding Energy

Determine the binding energy for the nuclide in:

a. joules per mole of nuclei
b. joules per nucleus
c. MeV per nucleus

Solution

The mass defect for a $^{4}_{2}\mathrm{He}$ nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).

a. First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of $3.05 \times 10^{-5}\ \mathrm{kg/mol}$. Substituting this quantity into the mass-energy equivalence equation yields:

$$E = mc^2 = \frac{3.05 \times 10^{-5} kg}{mol} \times \left(\frac{2.998 \times 10^{8} m}{s}\right)^2 = 2.74 \times 10^{12}\ \mathrm{kg\ m^2 s^{-2} mol^{-1}}$$
$$= 2.74 \times 10^{12}\ \mathrm{J\ mol^{-1}} = 2.74\ \mathrm{TJ\ mol^{-1}}$$

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

b. The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$E = 2.74 \times 10^{12}\ \mathrm{J\ mol^{-1}} \times \frac{1\ \mathrm{mol}}{6.022 \times 10^{23}\ \mathrm{nuclei}}$$
$$= 4.55 \times 10^{-12}\ \mathrm{J} = 4.55\ \mathrm{pJ}$$

c. Recall that $1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$. Using the binding energy computed in part (b):

$$E = 4.55 \times 10^{-12}\ \mathrm{J} \times \frac{1\ \mathrm{eV}}{1.602 \times 10^{-19}\ \mathrm{J}} = 2.84 \times 10^{7}\ \mathrm{eV} = 28.4\ \mathrm{MeV}$$

Exercise 19.3.1

What is the binding energy for the $^{19}_{9}\mathrm{F}$ nuclide (atomic mass: $18.9984\ \mathrm{amu}$) in MeV per nucleus?

Answer

148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the **band of stability** (also called the belt, zone, or valley of stability). The straight line in Figure 19.3.1 represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the

lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

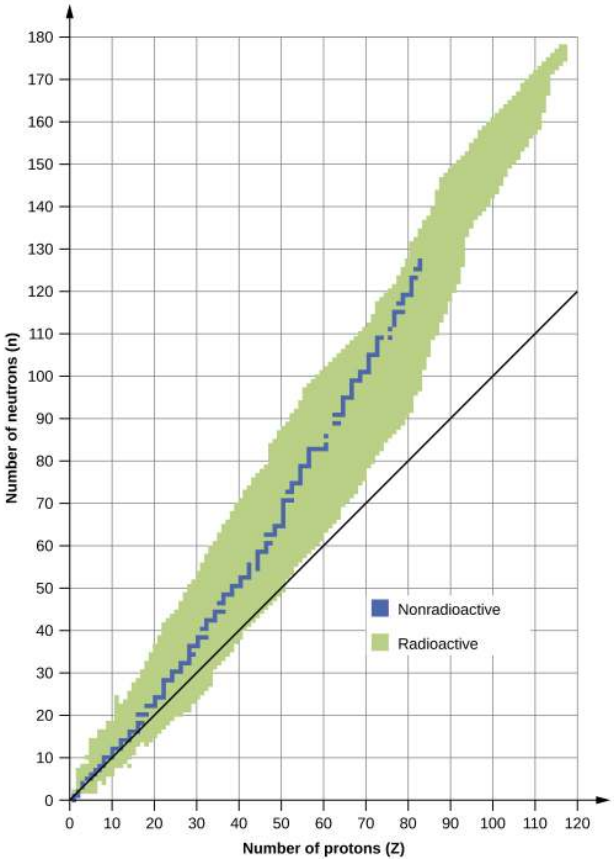


Figure **19.3.1**: This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit **radioactivity**. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or **radioisotope**) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (see Table **19.3.1**). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as and are called “double magic” and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Table **19.3.1**: Stable Nuclear Isotopes

https://chem.libretexts.org/@go/page/548630

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

The relative stability of a nucleus is correlated with its **binding energy per nucleon**, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, we saw in Example **19.3.2** that the binding energy for a $^{4}_{2}\mathrm{He}$ nucleus is 28.4 MeV. The *binding energy per nucleon* for a $^{4}_{2}\mathrm{He}$ nucleus is therefore:

In Example **19.3.3**, we learn how to calculate the binding energy per nucleon of a nuclide on the curve shown in Figure **19.3.2**.

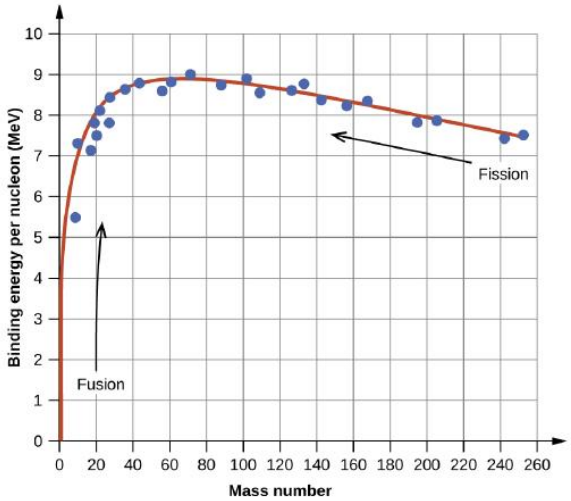


Figure **19.3.2**: The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

Example 19.3.3: Calculation of Binding Energy per Nucleon

The iron nuclide atom $^{56}_{26}\mathrm{Fe}$ lies near the top of the binding energy curve (Figure **19.3.2**) and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide $^{56}_{26}\mathrm{Fe}$ (atomic mass of 55.9349 amu)?

Solution

As in Example **19.3.2**, we first determine the mass defect of the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an $^{56}_{26}\mathrm{Fe}$ atom:

$$\begin{aligned}\text{Mass defect} &= [(26 \times 1.0073\,\text{amu}) + (30 \times 1.0087\,\text{amu}) + (26 \times 0.00055\,\text{amu})] - 55.9349 amu \\ &= 56.4651\,\text{amu} - 55.9349\,\text{amu} \\ &= 0.5302\,\text{amu}\end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$\begin{aligned}E = mc^2 &= 0.5302\,\text{amu} \times \left(\frac{1.6605 \times 10^{-27}\,\text{kg}}{1\,\text{amu}}\right) \times \left(2.998 \times 10^{8}\,\text{m/s}\right)^2 \\ &= 7.913 \times 10^{-11}\,\text{kg} \cdot \text{m}^2/\text{s}^2 \\ &= 7.913 \times 10^{-11}\,\text{J}\end{aligned}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913 \times 10^{-11}\,\text{J} \times \frac{1\,\text{MeV}}{1.602 \times 10^{-13}\,\text{J}} = 493.9\,\text{MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

Note that this is almost 25% larger than the binding energy per nucleon for $\mathbf{^4_2He}$.

$$\textbf{Binding energy per nucleon} = \frac{493.9\,\text{MeV}}{56} = 8.820\,\text{MeV/ nucleon}$$

(Note also that this is the same process as in Example **19.3.1**, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

? Exercise 19.3.1

What is the binding energy per nucleon in $\mathbf{^{19}_9F}$ (atomic mass, 18.9984 amu)?

Answer

$7.810\,\text{MeV/nucleon}$

This page titled 19.3: Nuclear Structure and Stability is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **21.1: Nuclear Structure and Stability** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

19.4: Nuclear Equations

Learning Objectives

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

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Figure **19.4.1**. Protons ($_1^1\mathrm{p}$, also represented by the symbol $_1^1\mathrm{H}$) and neutrons ($_0^1\mathrm{n}$) are the constituents of atomic nuclei, and have been described previously. **Alpha particles** ($_2^4\mathrm{He}$, also represented by the symbol $_2^4\alpha$) are high-energy helium nuclei. **Beta particles** ($_{-1}^0\beta$, also represented by the symbol $_1^0\mathrm{e}$) are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. **Positrons** ($_{+1}^0\mathrm{e}$, also represented by the symbol $_1^0\beta$) are positively charged electrons ("anti-electrons"). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized $_2^4\mathrm{He}$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Name	Symbol(s)	Representation	Description
Alpha particle	$_2^4\mathrm{He}$ or $_2^4\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$_{-1}^0\mathrm{e}$ or $_{-1}^0\beta$		(High-energy) electrons
Positron	$_{+1}^0\mathrm{e}$ or $_{+1}^0\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	$_1^1\mathrm{H}$ or $_1^1\mathrm{p}$		Nuclei of hydrogen atoms
Neutron	$_0^1\mathrm{n}$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Figure **19.4.1**: Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of **antimatter**, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of **gamma rays** (γ)—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$$_{-1}{}^0\mathrm{e} + {}_{+1}{}^0\mathrm{e} \longrightarrow \gamma + \gamma$$

As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are a type of high energy electromagnetic radiation produced when a nucleus undergoes a transition

from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of nucleons (subatomic particles within the atoms' nuclei) rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}\text{O}$ is a product of the nuclear reaction of $^{14}_{7}\text{N}$ and $^{4}_{2}\text{He}$ if we knew that a proton, $^{1}_{1}\text{H}$, were one of the two products. Example 19.4.1 shows how we can identify a nuclide by balancing the nuclear reaction.

Example 19.4.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 ($^{25}_{12}\text{Mg}$) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\text{Mg} + {}^{4}_{2}\text{He} \longrightarrow {}^{1}_{1}\text{H} + {}^{A}_{Z}\text{X}$$

where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = A + 1$$

or $A = 28$.

Similarly, the charges must balance, so:

$$12 + 2 = Z + 1$$

and $Z = 13$.

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\text{Al}$

Exercise 19.4.1

The nuclide $^{125}_{53}\text{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$^{125}_{53}\text{I} + {}^{0}_{-1}\text{e} \longrightarrow {}^{125}_{52}\text{Te}$$

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\mathrm{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\mathrm{H} + {}^{97}_{42}\mathrm{Mo} \longrightarrow 2{}^{1}_{0}\mathrm{n} + {}^{97}_{43}\mathrm{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\mathrm{U} + {}_{0}{}^{1}\ \mathrm{n} \longrightarrow {}^{87}_{35}\mathrm{Br} + {}^{146}_{57}\mathrm{La} + 3{}^{1}_{0}\mathrm{n}$$

This page titled 19.4: Nuclear Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **21.2: Nuclear Equations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

19.5: Radioactive Decay

Learning Objectives

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

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term “radioactivity,” and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is **radioactive decay**. The unstable nuclide is called the **parent nuclide**; the nuclide that results from the decay is known as the **daughter nuclide**. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure **19.5.1**).

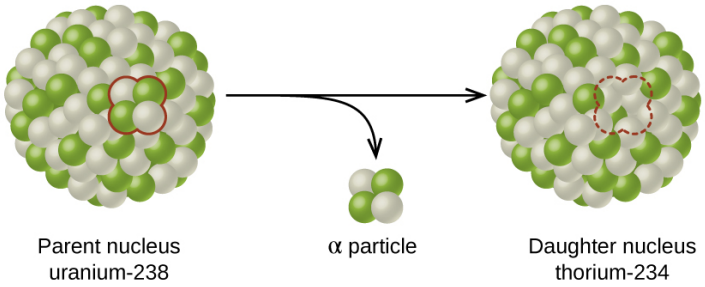


Figure **19.5.1**: A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

Link to Learning

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

Types of Radioactive Decay

Ernest Rutherford’s experiments involving the interaction of radiation with a magnetic or electric field (Figure **19.5.2**) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

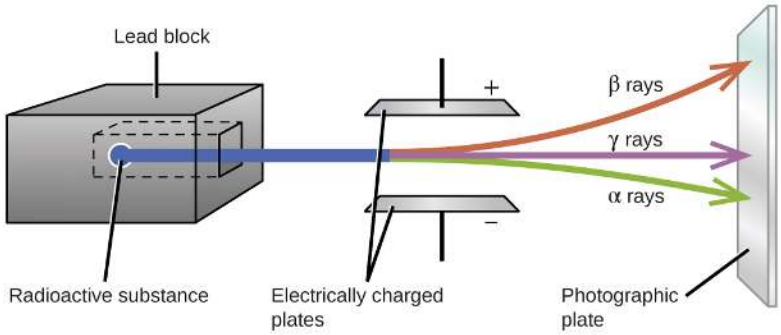


Figure **19.5.2**: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{206}_{82}\text{Pb}$$

or

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\alpha^{+} {}^{206}_{82}\text{Pb}$$

Alpha decay occurs primarily in heavy nuclei ($A > 200$, $Z > 83$). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below the band of stability (refer to Figure 21.2), the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron (i.e., a β particle) from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\text{e} + {}^{131}_{54}\text{Xe}$$

or

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\beta^{+} {}^{131}_{54}\text{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\text{Co}^{*} \longrightarrow {}^{0}_{0}\gamma^{+} {}^{60}_{27}\text{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^{+} decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_{8}\text{O} \longrightarrow {}^{0}_{+1}\text{e} + {}^{15}_{7}\text{N}$$

or

$$^{15}_{8}\text{O} \longrightarrow {}^{0}_{+1}\beta^{+} {}^{15}_{7}\text{N}$$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{40}_{18}\mathrm{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

Figure 19.5.3 summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

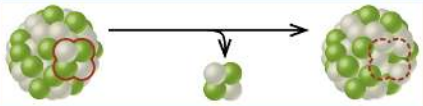
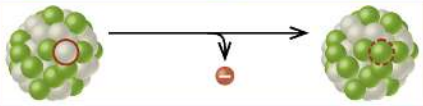
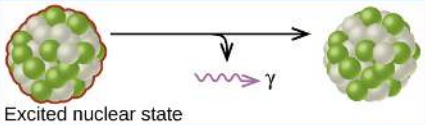
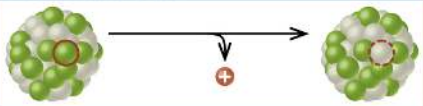
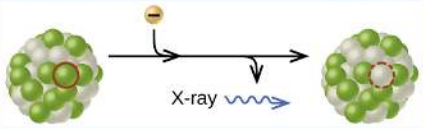
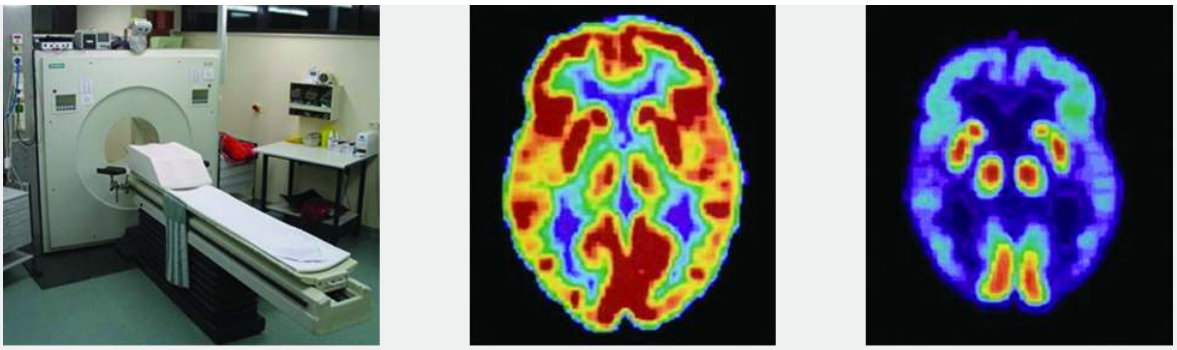
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{A-4}_{Z-2}\mathrm{Y}$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Z+1}\mathrm{Y}$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}\mathrm{Y}$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{+1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1

Figure 19.5.3: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

Chemistry in Everyday Life: PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient's body function (Figure 19.5.4). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This "tagged" compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.



(a) (b) (c)

Figure **19.5.4**: A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

For example, F-18 is produced by proton bombardment of ^{18}O

$$^{18}_{8}O + {}_{1}^{1}p \longrightarrow {}^{18}_{9}F + {}_{0}^{1}n$$

and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or **radioactive decay series**. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure **19.5.5**). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

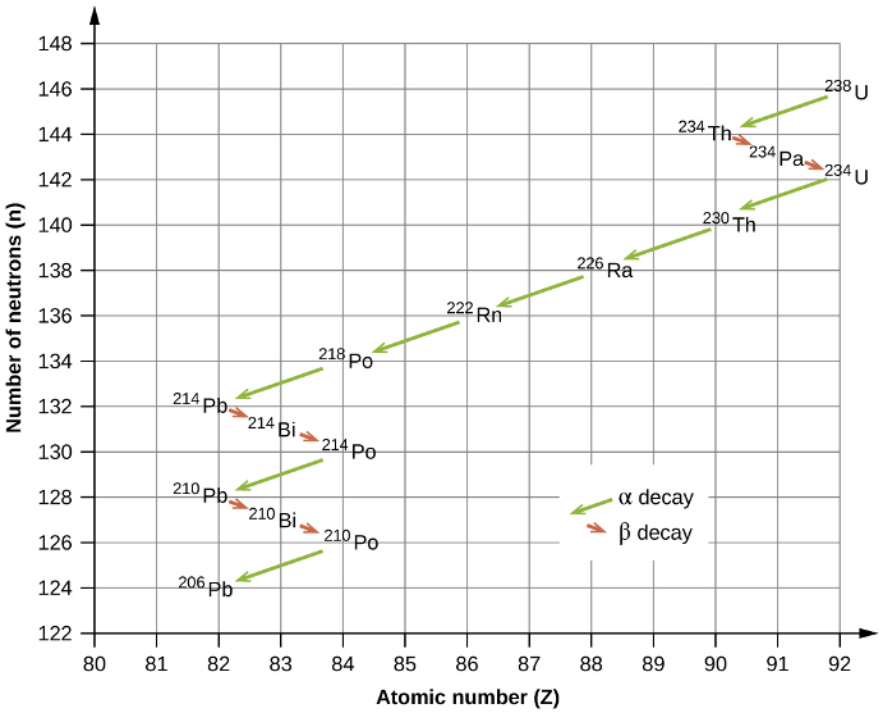


Figure **19.5.5**: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, coba source, since half of the nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

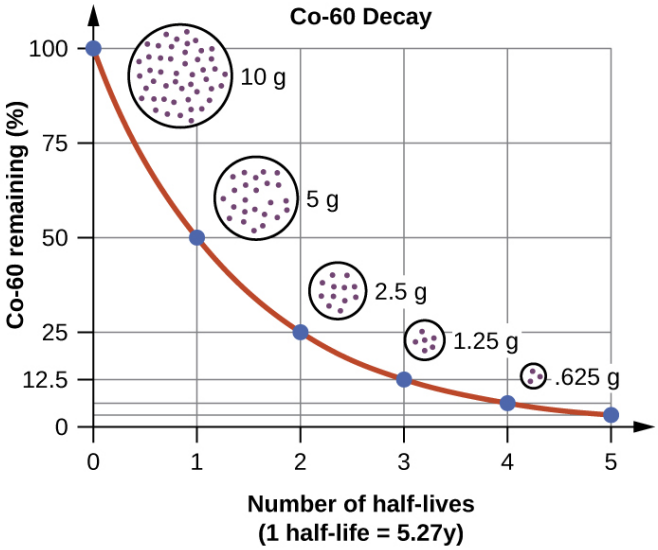


Figure **19.5.6**: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, N, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the **activity** of the radioactive sample. The rate for radioactive decay is:

$$\text{decay rate} = \lambda N$$

with λ = the decay constant for the particular radioisotope.

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

or

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, N, and time are:

$$N_t = N_0 e^{-\lambda t} \tag{19.5.1}$$

or

$$t = -\frac{1}{\lambda} \ln \left(\frac{N_t}{N_0} \right)$$

Example 19.5.1: Rates of Radioactive Decay

$^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce $^{60}_{28}\text{Co}$

a. What is the decay constant for the radioactive disintegration of cobalt-60?
b. Calculate the fraction of a sample of the $^{60}_{27}\text{Co}$ isotope that will remain after 15 years.
c. How long does it take for a sample of $^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution a

The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27y} = 0.132y^{-1}$$

Solution b

The fraction of $^{60}_{27}\text{Co}$ that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship in Equation 19.5.1 ($N_t = N_0 e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15\,\text{y})} = 0.138$$

The fraction of $^{60}_{27}\text{Co}$ that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the original $^{60}_{27}\text{Co}$ present will remain after 15 years.

Solution c

2.00% of the original amount of $^{60}_{27}\text{Co}$ is equal to 0.0200 N_0. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\,\text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6y$$

? Exercise 19.5.1

Radon-222, $^{222}_{86}\text{Rn}$ has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer

11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\text{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\text{Ra}$ is 24,000 years; $^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table 19.5.1, and others are listed in Appendix M.

Table 19.5.1: Half-lives of Radioactive Isotopes Important to Medicine

Type[1]	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of “dating” the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\text{C}$ which constitutes about 99% of the carbon on earth; $^{13}_{6}\text{C}$, about 1% of the total; and trace amounts of $^{14}_{6}\text{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\text{N} + ^{1}_{0}\text{n} \longrightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}\text{CO}_2$ to $^{12}_{6}\text{CO}_2$ depends on the ratio of $^{14}_{6}\text{CO}$ to $^{12}_{6}\text{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\text{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}\text{CO}_2$ and $^{14}_{6}\text{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\text{C} : ^{12}_{6}\text{C}$ ratio found in a living plant is the **same** as the $^{14}_{6}\text{C} : ^{12}_{6}\text{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\text{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\text{C} \longrightarrow ^{14}_{7}\text{N} + ^{0}_{-1}\text{e}$$

Thus, the ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure **19.5.7**: visually depicts this process.

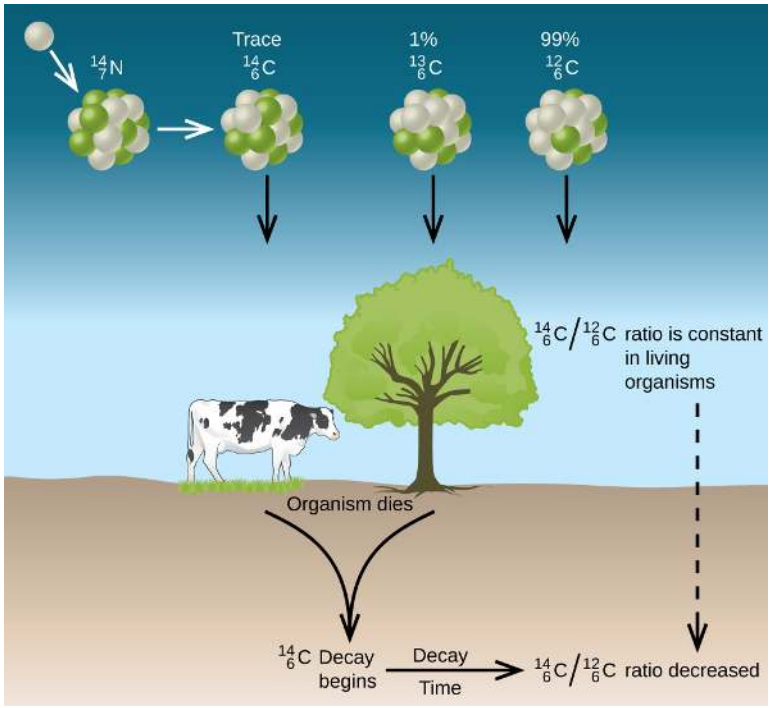


Figure **19.5.7**: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of being 5730 years, if the ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Link to Learning

Visit this website to perform simulations of radiometric dating.

Example 19.5.2: Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, N, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript t represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\,\text{y}} = 1.21 \times 10^{-4}\,\text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right) = -\frac{1}{1.21 \times 10^{-4}\,\text{y}^{-1}}\ln\left(\frac{10.8\ \cancel{\text{dis/min/g C}}}{13.6\ \cancel{\text{dis/min/g C}}}\right) = 1910\,\text{y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 19.5.8).



Figure 19.5.8: Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Exercise 19.5.1

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer

about 3350 years ago, or approximately 1340 BC

There have been some significant, well-documented changes to the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely $^{12}_{6}\text{C}$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the $^{14}_{6}\text{C}$ has decayed), the ratio of $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ in the atmosphere may be changing. This manmade increase in $^{12}_{6}\text{C}$ in the atmosphere causes the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate

correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Example 19.5.3: Radioactive Dating of Rocks

An igneous rock contains $9.58 \times 10^{-5}\ \text{g}$ of U-238 and $2.51 \times 10^{-5}\ \text{g}$ of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5}\ \cancel{\text{g U}} \times \left(\frac{1\ \text{mol U}}{238\ \cancel{\text{g U}}}\right) = 4.03 \times 10^{-7}\ \text{mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5}\ \cancel{\text{g Pb}} \times \left(\frac{1\ \cancel{\text{mol Pb}}}{206\ \cancel{\text{g Pb}}}\right) \times \left(\frac{1\ \text{mol U}}{1\ \cancel{\text{mol Pb}}}\right) = 1.22 \times 10^{-7}\ \text{mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7}\ \text{mol U} + 1.22 \times 10^{-7}\ \text{mol U} = 5.25 \times 10^{-7}\ \text{mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of $4.5 \times 10^9\ \text{y}$, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9\ \text{y}} = 1.54 \times 10^{-10}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10}\ \text{y}^{-1}} \ln\left(\frac{4.03 \times 10^{-7}\ \cancel{\text{mol U}}}{5.25 \times 10^{-7}\ \cancel{\text{mol U}}}\right) = 1.7 \times 10^{9}\ \text{y}$$

Therefore, the rock is approximately 1.7 billion years old.

? Exercise 19.5.1

A sample of rock contains 6.14×10^{-4} g of Rb-87 and $3.51 \times 10^{-5} g$ of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7×10^{10} y.)

Answer

3.7 10^9 y

Footnotes

- 1The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

This page titled 19.5: Radioactive Decay is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **21.3: Radioactive Decay** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

19.6: Transmutation and Nuclear Energy

Learning Objectives

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

- Describe the synthesis of transuranium nuclides
- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission and fusion reactors

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Scientists learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

The $^{17}_{8}\text{O}$ and $^{14}_{7}\text{N}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules.

When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

Chemistry in Everyday Life: CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure **19.6.1**). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure **19.6.1**: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Link to Learning

Famous physicist Brian Cox talks about his work on the Large Hadron Collider at CERN, providing an entertaining and engaging tour of this massive project and the physics behind it.

View a short video from CERN, describing the basics of how its particle accelerators work.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$\begin{gathered} {}^{238}_{92}\mathrm{U} + {}_{0}{}^{1}\,\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \\ {}^{239}_{92}\mathrm{U} \longrightarrow {}^{239}_{93}\,\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \quad \text{half-life} = 23.5\ \text{min} \\ {}^{239}_{93}\,\mathrm{Np} \longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e} \quad \text{half-life} = 2.36\ \text{days} \end{gathered} \tag{19.6.1}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the fission of U-235. Additional neutrons are released during this fission process (see the next section), some of which combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. These processes are summarized in the equation:

$$ {}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\,\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu} \tag{19.6.2}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called **transuranium elements**. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 21.3.

Table 21.3: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$
einsteinium	Es	99	$^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	$^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	$^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4{}^{1}_{0}\text{n}$ $^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4{}^{1}_{0}\text{n}$
seaborgium	Sg	106	$^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3{}^{1}_{0}\text{n}$
meitnerium	Mt	107	$^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56 (see Figure 21.3). Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure **19.6.2**.

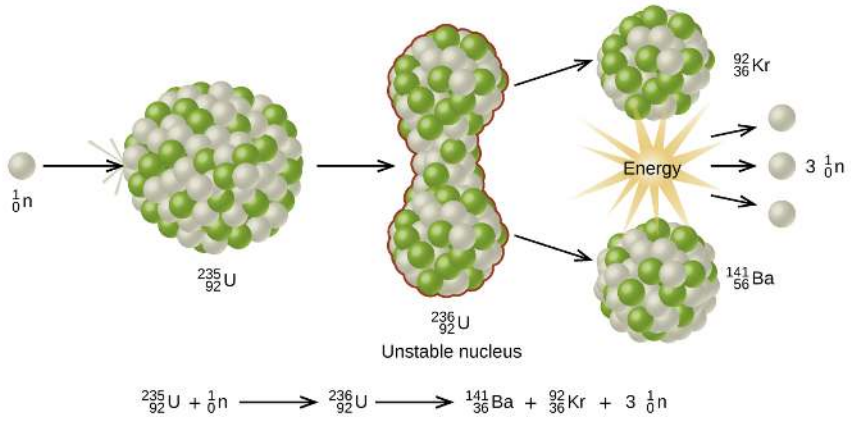


Figure **19.6.2**: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its

fission products and their yields, are shown in Figure **19.6.3**. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

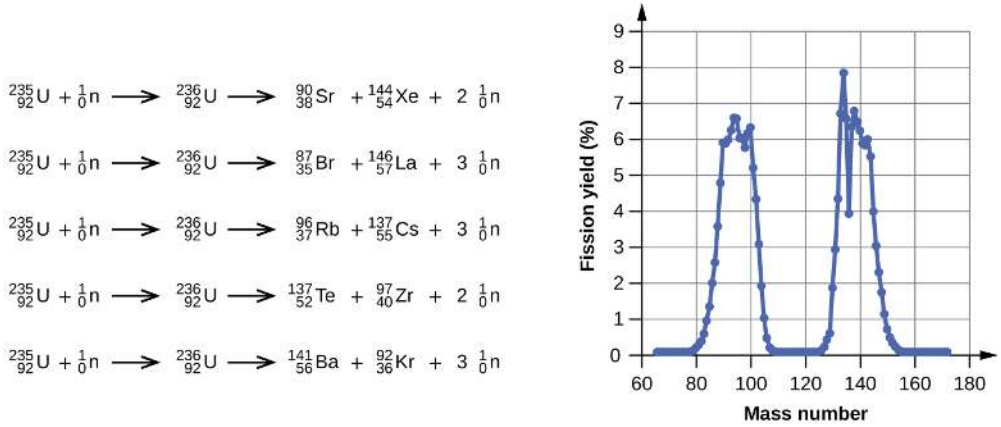


Figure **19.6.3**: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

Link to Learning

View this link to see a simulation of nuclear fission.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8 10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear **chain reaction** (see Figure **19.6.4**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

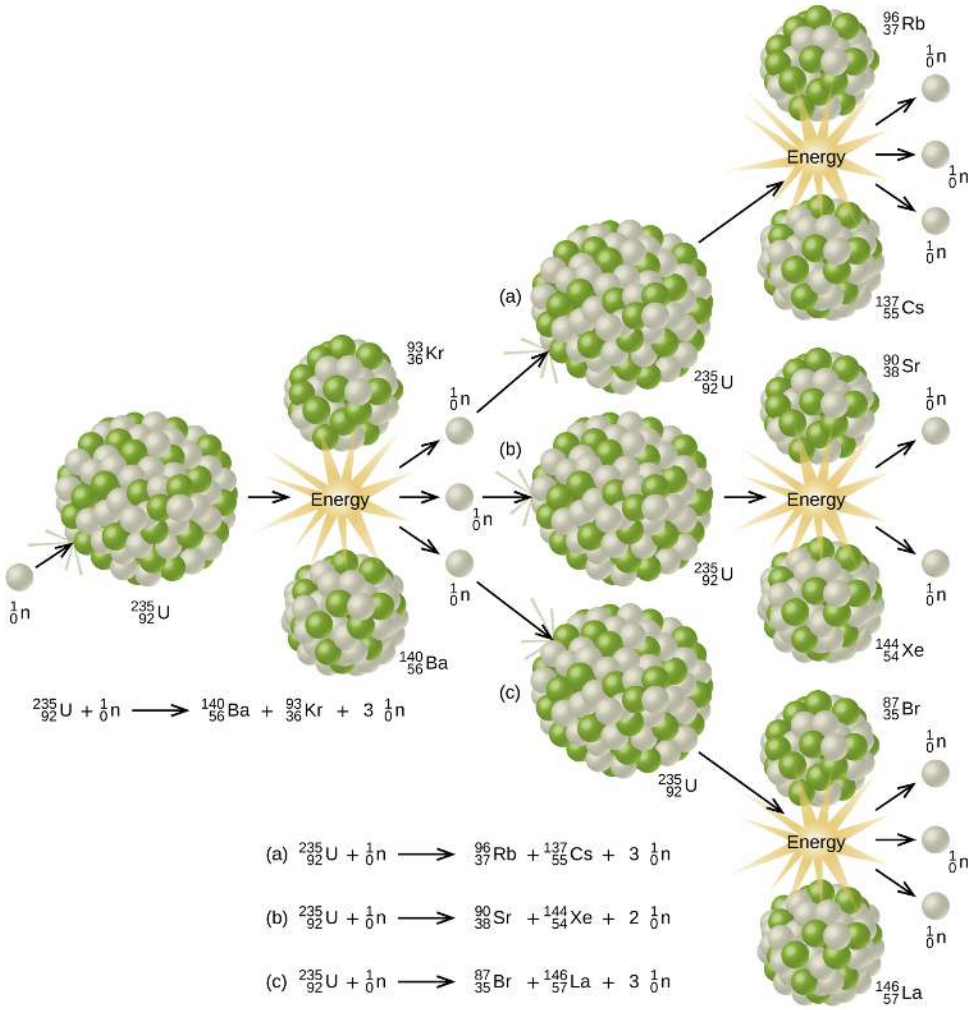


Figure **19.6.4**: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be **fissile** or **fissionable**. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a **critical mass**. An amount of fissionable material that cannot sustain a chain reaction is a **subcritical mass**. An amount of material in which there is an increasing rate of fission is known as a **supercritical mass**. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure **19.6.5**).

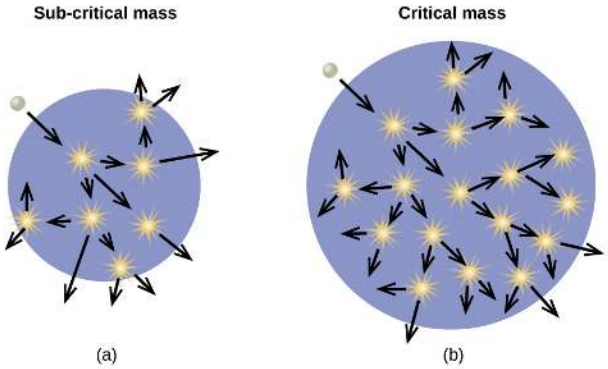


Figure 19.6.5: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 19.6.6) contains several pounds of fissionable material, $^{235}_{92}\mathrm{U}$ or $^{239}_{94}\mathrm{Pu}$ a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

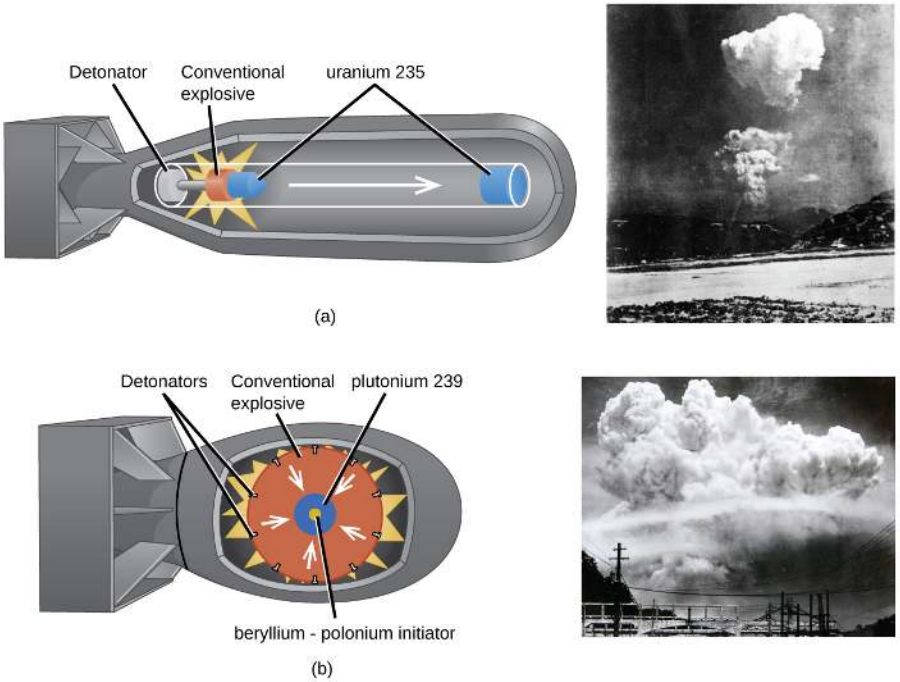


Figure 19.6.6: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 9, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a **nuclear reactor** (Figure 19.6.7). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission

reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

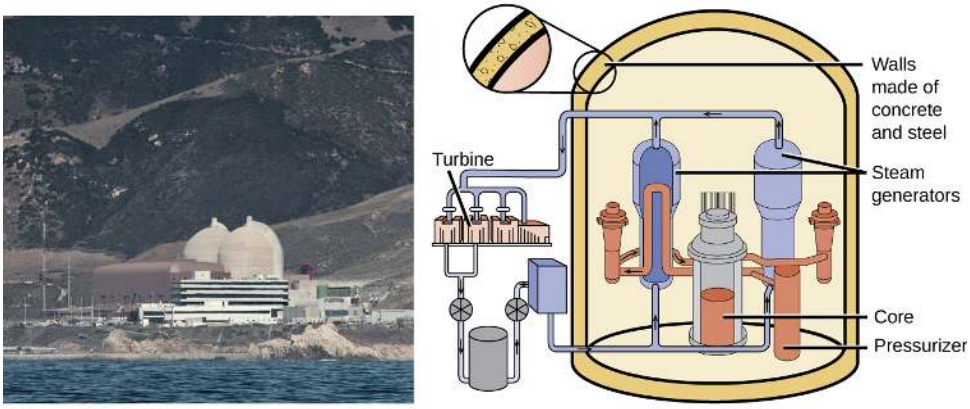


Figure 19.6.7: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by "Mike" Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham's law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (refer back to Figure 19.6.5). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A **nuclear moderator** is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure 19.6.8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} \tag{19.6.3}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

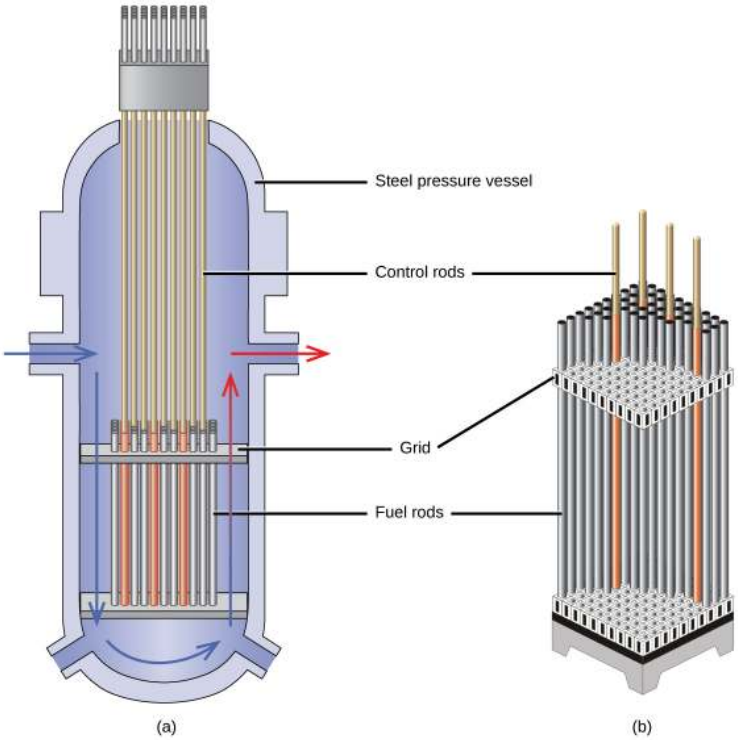


Figure 19.6.8: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, http://glossary.periodni.com/glossar...en=control+rod)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a **containment system** (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

Link to Learning

Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Chemistry in Everyday Life: Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr(s) + 2\,H_2O(g) \longrightarrow ZrO_2(s) + 2\,H_2(g)}$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure **19.6.9**).

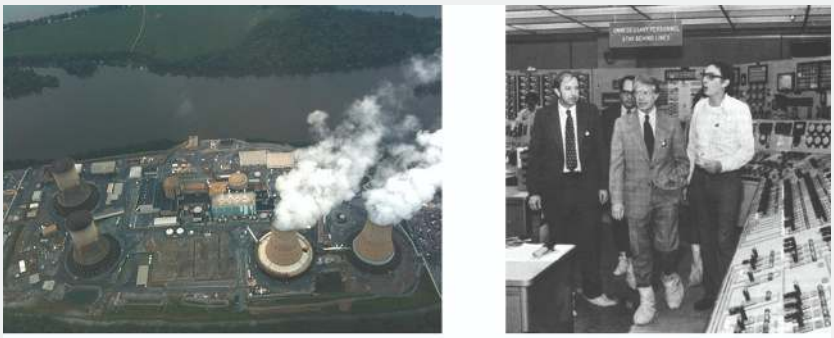


Figure **19.6.9**: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute

radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 19.6.10).



Figure 19.6.10: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Link to Learning

Explore the information in this link to learn about the approaches to nuclear waste management.

Nuclear Fusion and Fusion Reactors

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{e}^{+}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6 10^{11} kJ of energy per mole of \({ }_2^4 \mathrm{He}\) produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8 10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}\mathrm{H}$, and a triton, ${}^{3}_{1}\mathrm{H}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{19.6.4}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69 10^{9} kilojoules per mole of \({ }_2^4 \mathrm{He}\) formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

Another much more beneficial way to create fusion reactions is in a **fusion reactor**, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 19.6.11). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

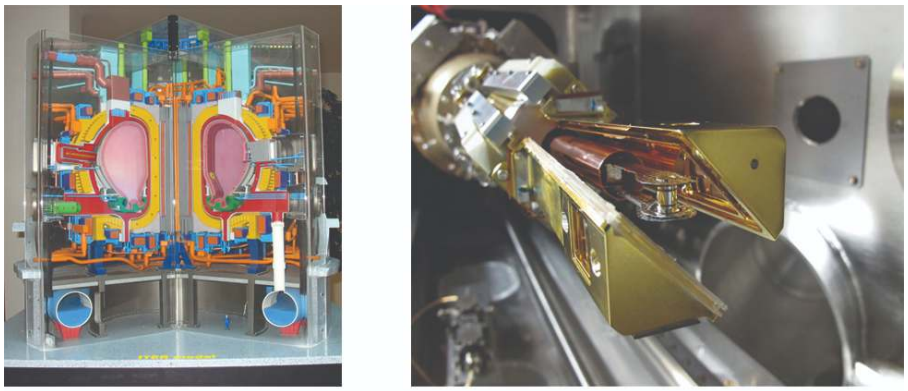


Figure 19.6.11: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

This page titled 19.6: Transmutation and Nuclear Energy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **21.4: Transmutation and Nuclear Energy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

19.7: Uses of Radioisotopes

Learning Objectives

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

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioimmunossays (RIA), for example, rely on radioisotopes to detect the presence and/or concentration of certain antigens. Developed by Rosalyn Sussman Yalow and Solomon Berson in the 1950s, the technique is known for extreme sensitivity, meaning that it can detect and measure very small quantities of a substance. Prior to its discovery, most similar detection relied on large enough quantities to produce visible outcomes. RIA revolutionized and expanded entire fields of study, most notably endocrinology, and is commonly used in narcotics detection, blood bank screening, early cancer screening, hormone measurement, and allergy diagnosis. Based on her significant contribution to medicine, Yalow received a Nobel Prize, making her the second woman to be awarded the prize for medicine.

Radioisotopes have revolutionized medical practice (see Appendix M), where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), thallium-201 ($^{201}_{81}\mathrm{Tl}$), iodine-131 ($^{131}_{53}\mathrm{I}$), and sodium-24 ($^{24}_{11}\mathrm{Na}$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure **19.7.1**) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.



Figure **19.7.1**: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure **19.7.2**). The parent nuclide Mo-99 is part of a molybdate ion, MoO_4^{2-}; when it decays, it forms the pertechnetate ion, TcO_4^-. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.

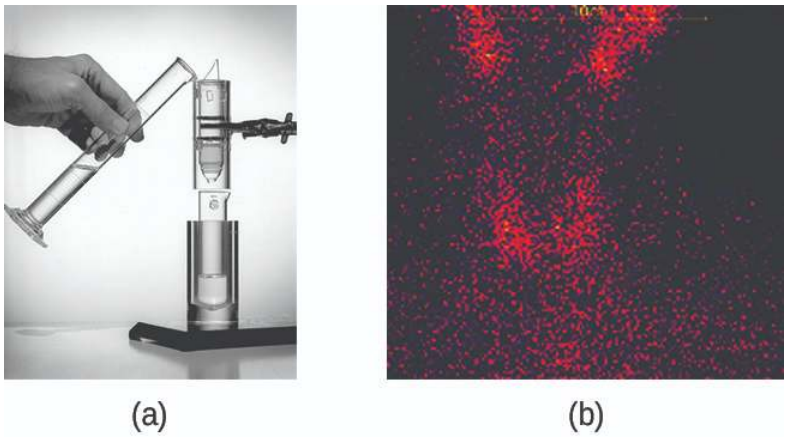


Figure **19.7.2**: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The is retained by the matrix in the column, whereas the passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure **19.7.3**). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

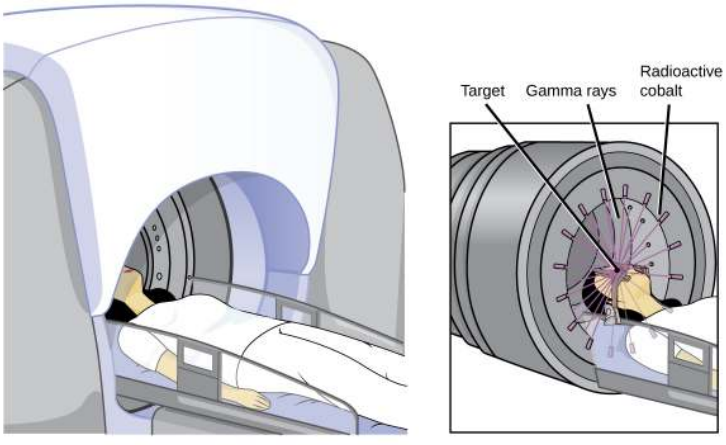


Figure **19.7.3**: The cartoon in (a) shows a coba machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$^{59}_{27}\mathrm{Co} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{60}_{27}\mathrm{Co} \rightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}\beta + 2{}^{0}_{0}\gamma \tag{19.7.1}$$

The overall decay scheme for this is shown graphically in Figure 19.7.4.

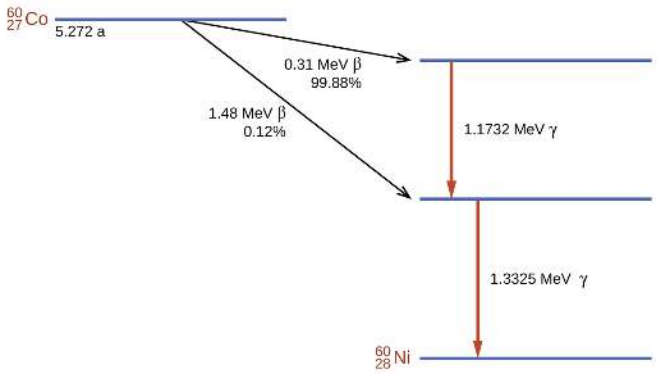


Figure 19.7.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6CO_2(g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (s) + 6O_2\ (g), \tag{19.7.2}$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of ($^{14}_{6}C$). At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure 19.7.5). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

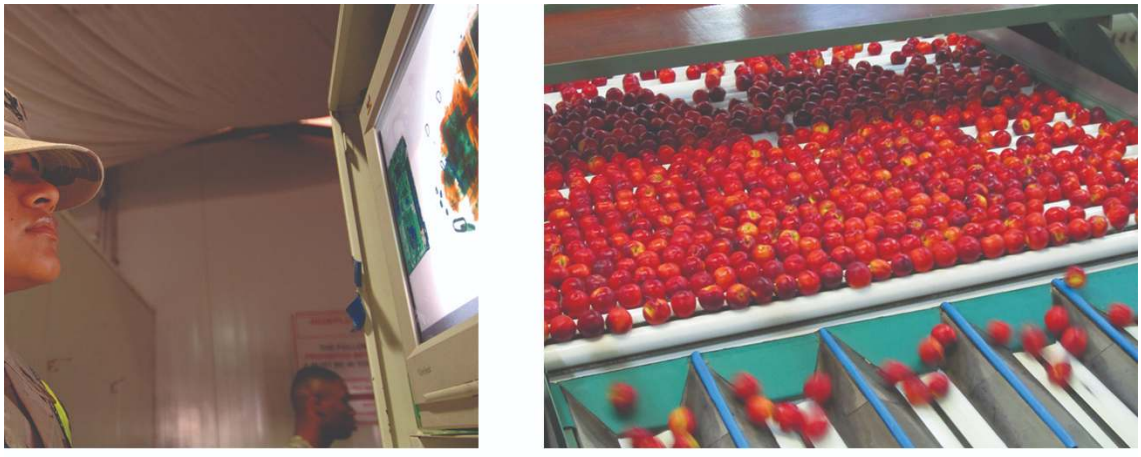


Figure 19.7.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 19.7.6). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a

potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

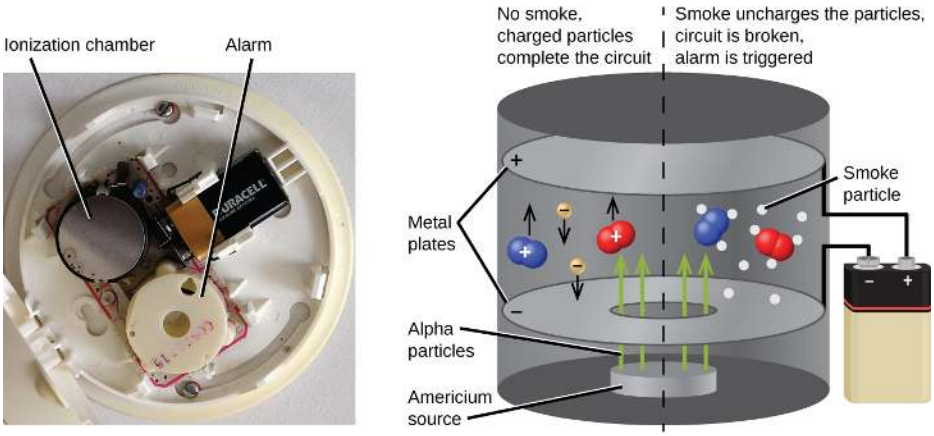


Figure 19.7.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

This page titled 19.7: Uses of Radioisotopes is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **21.5: Uses of Radioisotopes** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

19.8: Biological Effects of Radiation

Learning Objectives

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

- Describe the biological impact of ionizing radiation
- Define units for measuring radiation exposure
- Explain the operation of common tools for detecting radioactivity
- List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 19.8.1).

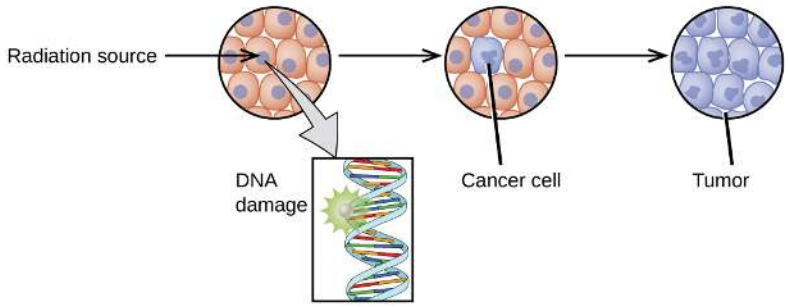


Figure 19.8.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Ionizing and Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 19.8.2).

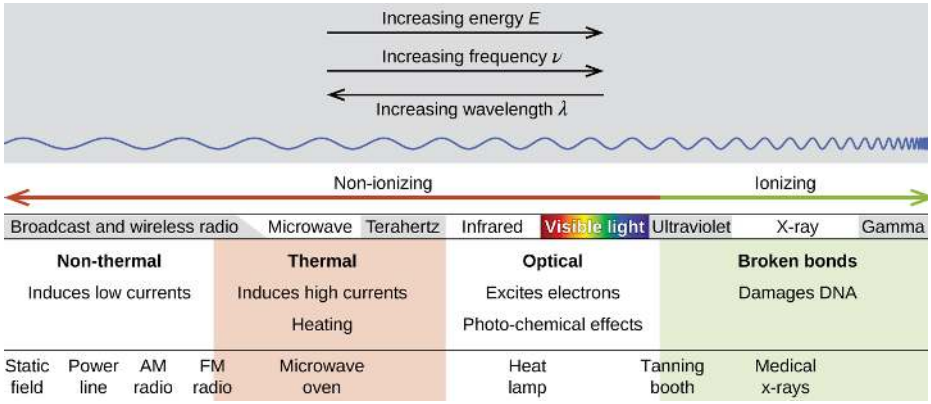


Figure 19.8.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the

beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$

Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in Figure 21.32.

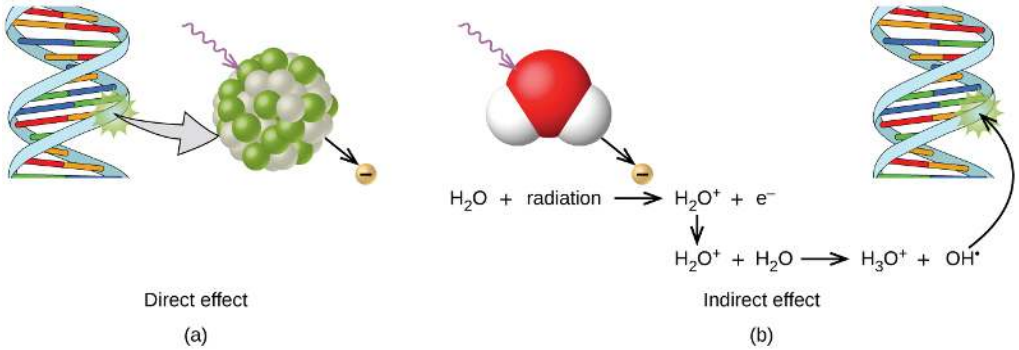


Figure 21.32 Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure **19.8.3**). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

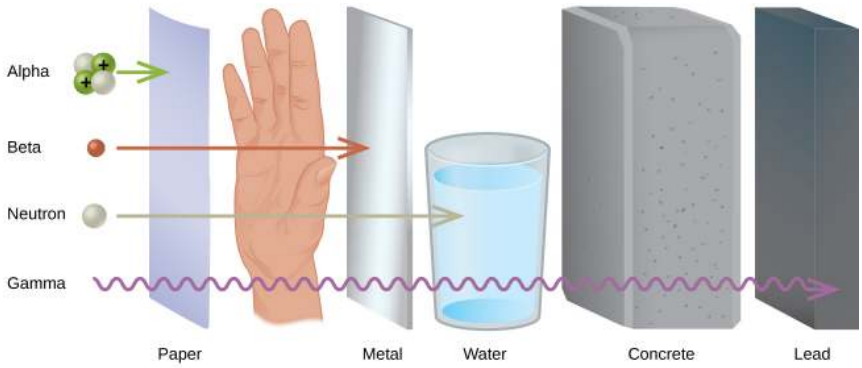


Figure 19.8.3: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

Chemistry in Everyday Life: Radon Exposure

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238 (Figure 21.9), which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 19.8.4).

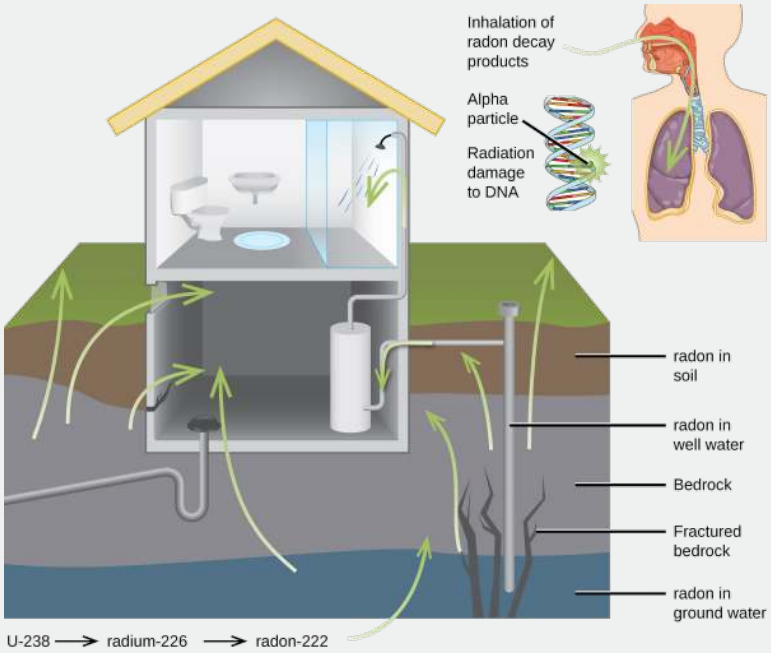


Figure 19.8.4: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 19.8.5). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

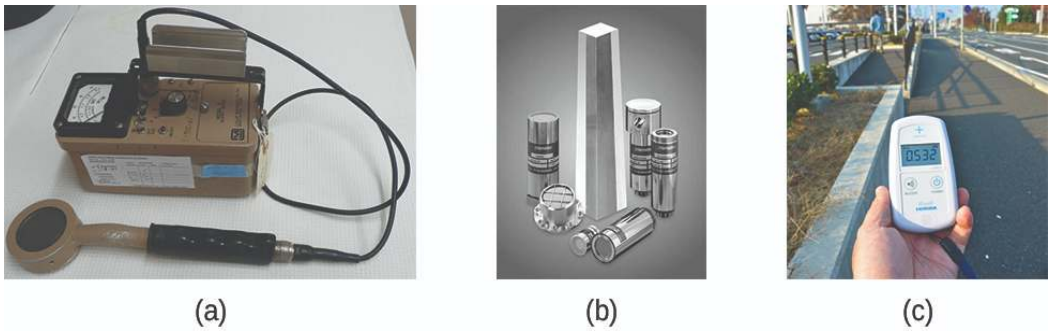


Figure 19.8.5: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons)

A variety of units are used to measure various aspects of radiation (Figure 19.8.6). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7 10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose. The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (100 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the RBE (for relative biological effectiveness) that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{19.8.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

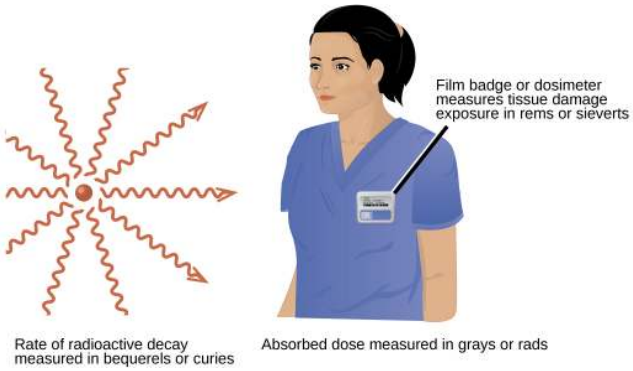


Figure 19.8.6: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.

Units of Radiation Measurement

Table 19.8.1 summarizes the units used for measuring radiation.

Table 19.8.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7 10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE Gy
	roentgen equivalent for man (rem)		Rem = RBE rad

Example 19.8.1: Amount of Radiation

Cobalt-60 ($t_{1/2} = 5.26\ y$) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity } = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\text{y}}\right) \times 5.00\ \text{g} = 0.659\frac{\text{g}}{\text{y}}\ \text{of Co } -60\ \text{that decay}$$

And to convert this to decays per second:

$$0.659\frac{\text{g}}{\text{y}} \times \frac{1\text{y}}{365\ \text{d}} \times \frac{1\ \text{d}}{24\ \text{h}} \times \frac{1\ \text{h}}{3600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$
$$= 2.10 \times 10^{14}\frac{\text{decay}}{\text{s}}$$

a. Since $1\ \text{Bq} = \frac{1\ \text{decay}}{\text{s}}$ the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

b. Since $1\text{Ci} = \frac{3.7\times10^{11}\ \text{decay}}{\text{s}}$ the activity in curie (Ci) is:

$$2.10 \times 10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{Ci}}{\frac{3.7\times10^{11}\ \text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\text{Ci}$$

Exercise 19.8.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2}$ = 12.32 y) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer

a. 3.56 10^{11} Bq;
b. 0.962 Ci

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure **19.8.7**: , the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

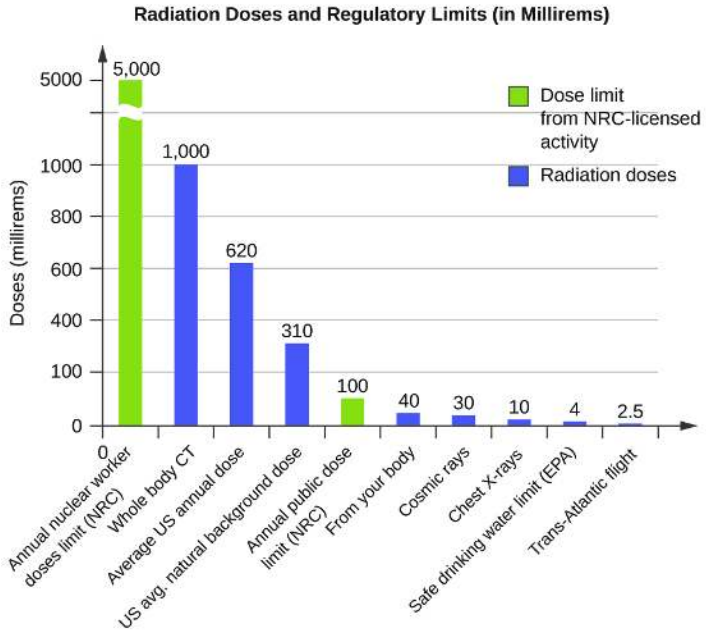


Figure **19.8.7**: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission)

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table **19.8.2**.

Table **19.8.2**: Health Effects of Radiation[2]

https://chem.libretexts.org/@go/page/548635

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Footnotes

- 2Source: US Environmental Protection Agency

This page titled 19.8: Biological Effects of Radiation is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **21.6: Biological Effects of Radiation** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

19.9: Key Terms

alpha (α) decay | loss of an alpha particle during radioactive decay

alpha particle | (α or or high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

band of stability | (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

becquerel (Bq) | SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

beta (β) decay | breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

beta particle | or or high-energy electron

binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

chemotherapy | similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

containment system | (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

control rod | material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7 10^{10} disintegrations/s

daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

electron volt (eV) | measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

external beam radiation therapy | radiation delivered by a machine outside the body

fissile (or fissionable) | when a material is capable of sustaining a nuclear fission reaction

fission | splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor | nuclear reactor in which fusion reactions of light nuclei are controlled

gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

gamma ray | (γ or short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

internal radiation therapy | (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

magic number | nuclei with specific numbers of nucleons that are within the band of stability

mass defect | difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

mass-energy equivalence equation | Albert Einstein’s relationship showing that mass and energy are equivalent

millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7 10^{10} disintegrations/s

nonionizing radiation | radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

nuclear binding energy | energy lost when an atom’s nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry | study of the structure of atomic nuclei and processes that change nuclear structure

nuclear fuel | fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator | substance that slows neutrons to a speed low enough to cause fission

nuclear reaction | change to a nucleus resulting in changes in the atomic number, mass number, or energy state

nuclear reactor | environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation | conversion of one nuclide into another nuclide

nucleon | collective term for protons and neutrons in a nucleus

nuclide | nucleus of a particular isotope

parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

positron or | antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

positron emission | (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

radiation dosimeter | device that measures ionizing radiation and is used to determine personal radiation exposure

radiation therapy | use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive decay | spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series | chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radioactive tracer | (also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

radioactivity | phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radiocarbon dating | highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of in the object vs. the ratio of in the present-day atmosphere

radioisotope | isotope that is unstable and undergoes conversion into a different, more stable isotope

radiometric dating | use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

reactor coolant | assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

relative biological effectiveness (RBE) | measure of the relative damage done by radiation

roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 100 rem = 1 Sv

scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

strong nuclear force | force of attraction between nucleons that holds a nucleus together

subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

supercritical mass | amount of material in which there is an increasing rate of fission

transmutation reaction | bombardment of one type of nuclei with other nuclei or neutrons

transuranium element | element with an atomic number greater than 92; these elements do not occur in nature

---

19.9: Key Terms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **21.7: Key Terms** is licensed CC BY 4.0.

19.10: Key Equations

$E = mc^2$

decay rate = λN

rem = RBE rad
Sv = RBE Gy

19.10: Key Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **21.8: Key Equations** is licensed CC BY 4.0.

19.11: Summary

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This “missing” mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein’s mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health

effects, from minor to severe, and including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source, and limiting time of exposure.

19.11: Summary is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **21.9: Summary** is licensed CC BY 4.0.

Index

A

acid ionization
14.4: Brønsted-Lowry Acids and Bases
acid ionization constant
14.6: Relative Strengths of Acids and Bases
acidic
14.5: pH and pOH
activated complex
12.8: Collision Theory
activation energy
12.8: Collision Theory
active electrode
18.5: Galvanic Cells
alkaline battery
18.8: Batteries and Fuel Cells
alpha decay
19.5: Radioactive Decay
alpha particle
19.4: Nuclear Equations
amphiprotic
14.4: Brønsted-Lowry Acids and Bases
amphoteric
14.4: Brønsted-Lowry Acids and Bases
anode
18.5: Galvanic Cells
antimatter
19.4: Nuclear Equations
Arrhenius equation
12.8: Collision Theory
autoionization
14.4: Brønsted-Lowry Acids and Bases
average rate
12.4: Chemical Reaction Rates

B

band of stability
19.3: Nuclear Structure and Stability
base ionization
14.4: Brønsted-Lowry Acids and Bases
base ionization constant
14.6: Relative Strengths of Acids and Bases
basic
14.5: pH and pOH
battery
18.8: Batteries and Fuel Cells
becquerel (unit)
19.8: Biological Effects of Radiation
beta decay
19.5: Radioactive Decay
beta particle
19.4: Nuclear Equations
bimolecular reaction
12.9: Reaction Mechanisms
binding energy per nucleon
19.3: Nuclear Structure and Stability
bomb calorimeter
16.3: Calorimetry
buffer
14.9: Buffers
buffer capacity
14.9: Buffers

C

calorie
16.2: Energy Basics
calorimeter
16.3: Calorimetry
calorimetry
16.3: Calorimetry
catalyst
12.5: Factors Affecting Reaction Rates
cathode
18.5: Galvanic Cells
cathodic protection
18.9: Corrosion
Cell Notation
18.5: Galvanic Cells
cell potential
18.5: Galvanic Cells
chain reaction
19.6: Transmutation and Nuclear Energy
chemical thermodynamics
16.4: Enthalpy
Chemotherapy
19.7: Uses of Radioisotopes
circuit
18.4: Review of Redox Chemistry
collision theory
12.8: Collision Theory
common ion effect
15.2: Precipitation and Dissolution
complex ion
15.3: Lewis Acids and Bases
concentration cell
18.7: Potential, Free Energy, and Equilibrium
conjugate acid
14.4: Brønsted-Lowry Acids and Bases
conjugate base
14.4: Brønsted-Lowry Acids and Bases
containment system
19.6: Transmutation and Nuclear Energy
control rod
19.6: Transmutation and Nuclear Energy
coordinate covalent bond
15.3: Lewis Acids and Bases
corrosion
18.9: Corrosion
critical mass
19.6: Transmutation and Nuclear Energy
curie (unit)
19.8: Biological Effects of Radiation
current
18.4: Review of Redox Chemistry

D

daughter nuclide
19.5: Radioactive Decay
diprotic acid
14.8: Polyprotic Acids
diprotic base
14.8: Polyprotic Acids
dissociation constant
15.3: Lewis Acids and Bases
dry cell
18.8: Batteries and Fuel Cells

E

electrical potential
18.4: Review of Redox Chemistry
electrical work
18.7: Potential, Free Energy, and Equilibrium
electrolysis
18.10: Electrolysis
electrolytic cell
18.10: Electrolysis
electron capture
19.5: Radioactive Decay
electron volt
19.3: Nuclear Structure and Stability
electroplating
18.10: Electrolysis
elementary reaction
12.9: Reaction Mechanisms
endothermic process
16.2: Energy Basics
energy
16.2: Energy Basics
enthalpy
16.4: Enthalpy
enthalpy change
16.4: Enthalpy
entropy
17.3: Entropy
equilibrium
13.2: Chemical Equilibria
equilibrium constant
13.3: Equilibrium Constants
exothermic process
16.2: Energy Basics
expansion work
16.4: Enthalpy
external beam radiation therapy
19.7: Uses of Radioisotopes

F

Faraday's constant
18.7: Potential, Free Energy, and Equilibrium
first law of thermodynamics
16.4: Enthalpy
fissile
19.6: Transmutation and Nuclear Energy
fission
19.6: Transmutation and Nuclear Energy
fissionable
19.6: Transmutation and Nuclear Energy
formation constant
15.3: Lewis Acids and Bases
frequency factor
12.8: Collision Theory
fuel cell
18.8: Batteries and Fuel Cells
fusion
19.6: Transmutation and Nuclear Energy

fusion reactor
19.6: Transmutation and Nuclear Energy

G

galvanic cell
18.5: Galvanic Cells
galvanized iron
18.9: Corrosion
gamma emission
19.5: Radioactive Decay
gamma ray
19.4: Nuclear Equations
Geiger counter
19.8: Biological Effects of Radiation
Gibbs free energy
17.5: Free Energy
gray (unit)
19.8: Biological Effects of Radiation

H

heat
16.2: Energy Basics
heat capacity
16.2: Energy Basics
Hess's law
16.4: Enthalpy
heterogeneous catalyst
12.10: Catalysis
heterogeneous equilibria
13.3: Equilibrium Constants
homogeneous catalyst
12.10: Catalysis
homogeneous equilibria
13.3: Equilibrium Constants
hydrocarbon
16.4: Enthalpy

I

inert electrode
18.5: Galvanic Cells
initial rate
12.4: Chemical Reaction Rates
instantaneous rate
12.4: Chemical Reaction Rates
integrated rate law
12.7: Integrated Rate Laws
intermediate
12.9: Reaction Mechanisms
internal energy
16.4: Enthalpy
internal radiation therapy
19.7: Uses of Radioisotopes
ionic solvent
18.10: Electrolysis
ionizing radiation
19.8: Biological Effects of Radiation

J

joule
16.2: Energy Basics

K

Kc
13.3: Equilibrium Constants
kinetic energy
16.2: Energy Basics
Kp
13.3: Equilibrium Constants

L

Law of Mass Action
13.3: Equilibrium Constants
Le Châtelier's principle
13.4: Shifting Equilibria - Le Chatelier’s Principle
lead acid battery
18.8: Batteries and Fuel Cells
leveling effect of water
14.6: Relative Strengths of Acids and Bases
Lewis acid
15.3: Lewis Acids and Bases
Lewis base
15.3: Lewis Acids and Bases
ligand
15.3: Lewis Acids and Bases
lithium ion battery
18.8: Batteries and Fuel Cells

M

magic number
19.3: Nuclear Structure and Stability
mass defect
19.3: Nuclear Structure and Stability
Method of Initial Rates
12.6: Rate Laws
microstates
17.3: Entropy
millicurie (unit)
19.8: Biological Effects of Radiation
molar solubility
15.2: Precipitation and Dissolution
molecularity
12.9: Reaction Mechanisms
monoprotic acid
14.8: Polyprotic Acids
multiple equilibrium
15.4: Coupled Equilibria

N

Nernst equation
18.7: Potential, Free Energy, and Equilibrium
neutral
14.5: pH and pOH
Nonionizing radiation
19.8: Biological Effects of Radiation
nonspontaneous process
17.2: Spontaneity
nuclear binding energy
19.3: Nuclear Structure and Stability
nuclear chemistry
19.3: Nuclear Structure and Stability
nuclear fuel
19.6: Transmutation and Nuclear Energy
nuclear moderator
19.6: Transmutation and Nuclear Energy
nuclear reaction
19.4: Nuclear Equations
nuclear reactor
19.6: Transmutation and Nuclear Energy
nuclear transmutation
19.6: Transmutation and Nuclear Energy
nucleon
19.3: Nuclear Structure and Stability
nutritional calorie
16.3: Calorimetry

O

overall reaction order
12.6: Rate Laws
overpotential
18.10: Electrolysis
oxyacid
14.6: Relative Strengths of Acids and Bases

P

parent nuclide
19.5: Radioactive Decay
particle accelerator
19.6: Transmutation and Nuclear Energy
percent of ionization
14.6: Relative Strengths of Acids and Bases
pH
14.5: pH and pOH
pOH
14.5: pH and pOH
position of equilibrium
13.4: Shifting Equilibria - Le Chatelier’s Principle
Positron
19.4: Nuclear Equations
positron emission
19.5: Radioactive Decay
potential energy
16.2: Energy Basics
primary battery
18.8: Batteries and Fuel Cells

R

radiation absorbed dose
19.8: Biological Effects of Radiation
radiation dosimeter
19.8: Biological Effects of Radiation
radiation therapy
19.7: Uses of Radioisotopes
radioactive decay
19.5: Radioactive Decay
radioactive decay series
19.5: Radioactive Decay
radioactive tracer
19.7: Uses of Radioisotopes
radioactivity
19.3: Nuclear Structure and Stability
radiocarbon dating
19.5: Radioactive Decay
radioisotope
19.3: Nuclear Structure and Stability
radiometric dating
19.5: Radioactive Decay

rate constant
12.6: Rate Laws
rate expression
12.4: Chemical Reaction Rates
rate law
12.6: Rate Laws
rate of reaction
12.4: Chemical Reaction Rates
reaction mechanism
12.9: Reaction Mechanisms
reaction order
12.6: Rate Laws
reaction quotient
13.3: Equilibrium Constants
reactor coolant
19.6: Transmutation and Nuclear Energy
relative biological effectiveness
19.8: Biological Effects of Radiation
Reversible Process
17.3: Entropy
reversible reaction
13.2: Chemical Equilibria
roentgen equivalent man
19.8: Biological Effects of Radiation

S

sacrificial anode
18.9: Corrosion
scintillation counter
19.8: Biological Effects of Radiation
second law of thermodynamics
17.4: The Second and Third Laws of Thermodynamics
secondary battery
18.8: Batteries and Fuel Cells
selective precipitation
15.2: Precipitation and Dissolution
sievert (unit)
19.8: Biological Effects of Radiation
solubility product
15.2: Precipitation and Dissolution
specific heat capacity
16.2: Energy Basics
spontaneous change
17.2: Spontaneity
standard cell potential
18.6: Electrode and Cell Potentials
standard enthalpy of combustion
16.4: Enthalpy
standard enthalpy of formation
16.4: Enthalpy
standard entropy
17.4: The Second and Third Laws of Thermodynamics
standard entropy change
17.4: The Second and Third Laws of Thermodynamics
standard free energy change
17.5: Free Energy
standard free energy of formation
17.5: Free Energy
standard hydrogen electrode
18.6: Electrode and Cell Potentials
standard reduction potential
18.6: Electrode and Cell Potentials
standard state
16.4: Enthalpy
state function
16.4: Enthalpy
stepwise ionization
14.8: Polyprotic Acids
stress
13.4: Shifting Equilibria - Le Chatelier’s Principle
strong nuclear force
19.3: Nuclear Structure and Stability
subcritical mass
19.6: Transmutation and Nuclear Energy
supercritical mass
19.6: Transmutation and Nuclear Energy
surroundings
16.3: Calorimetry
system
16.3: Calorimetry

T

temperature
16.2: Energy Basics
termolecular reaction
12.9: Reaction Mechanisms
thermal energy
16.2: Energy Basics
thermochemistry
16.2: Energy Basics
Third Law of Thermodynamics
17.4: The Second and Third Laws of Thermodynamics
titration curve
14.10: Acid-Base Titrations
transmutation reaction
19.6: Transmutation and Nuclear Energy
transuranium element
19.6: Transmutation and Nuclear Energy
triprotic acid
14.8: Polyprotic Acids

U

unimolecular reaction
12.9: Reaction Mechanisms

V

voltaic cell
18.5: Galvanic Cells

W

water gas shift reaction
13.3: Equilibrium Constants
work
16.2: Energy Basics

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: Chem 108: Textbook

Webpages: 100

All licenses found:

- CC BY 4.0: 89% (89 pages)
- Undeclared: 10% (10 pages)
- CC BY-SA 4.0: 1% (1 page)

By Page

- Chem 108: Textbook - *CC BY-SA 4.0*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 12: Kinetics - *CC BY 4.0*
    - 12.1: Introduction - *CC BY 4.0*
    - 12.2: Summary - *CC BY 4.0*
    - 12.3: Exercises - *CC BY 4.0*
    - 12.4: Chemical Reaction Rates - *CC BY 4.0*
    - 12.5: Factors Affecting Reaction Rates - *CC BY 4.0*
    - 12.6: Rate Laws - *CC BY 4.0*
    - 12.7: Integrated Rate Laws - *CC BY 4.0*
    - 12.8: Collision Theory - *CC BY 4.0*
    - 12.9: Reaction Mechanisms - *CC BY 4.0*
    - 12.10: Catalysis - *CC BY 4.0*
    - 12.11: Key Terms - *CC BY 4.0*
    - 12.12: Key Equations - *CC BY 4.0*
  - 13: Fundamental Equilibrium Concepts - *CC BY 4.0*
    - 13.1: Introduction - *CC BY 4.0*
    - 13.2: Chemical Equilibria - *CC BY 4.0*
    - 13.3: Equilibrium Constants - *CC BY 4.0*
    - 13.4: Shifting Equilibria - Le Chatelier's Principle - *CC BY 4.0*
    - 13.5: Equilibrium Calculations - *CC BY 4.0*
    - 13.6: Key Terms - *CC BY 4.0*
    - 13.7: Key Equations - *CC BY 4.0*
    - 13.8: Summary - *CC BY 4.0*
    - 13.9: Exercises - *CC BY 4.0*
  - 14: Acid-Base Equilibria - *CC BY 4.0*
    - 14.1: Introduction - *CC BY 4.0*
    - 14.2: Summary - *CC BY 4.0*
    - 14.3: Exercises - *CC BY 4.0*
    - 14.4: Brønsted-Lowry Acids and Bases - *CC BY 4.0*
    - 14.5: pH and pOH - *CC BY 4.0*
    - 14.6: Relative Strengths of Acids and Bases - *CC BY 4.0*
    - 14.7: Hydrolysis of Salt Solutions - *CC BY 4.0*
    - 14.8: Polyprotic Acids - *CC BY 4.0*
    - 14.9: Buffers - *CC BY 4.0*
    - 14.10: Acid-Base Titrations - *CC BY 4.0*
    - 14.11: Key Terms - *CC BY 4.0*
    - 14.12: Key Equations - *CC BY 4.0*
  - 15: Equilibria of Other Reaction Classes - *CC BY 4.0*
    - 15.1: Introduction - *CC BY 4.0*
    - 15.2: Precipitation and Dissolution - *CC BY 4.0*
    - 15.3: Lewis Acids and Bases - *CC BY 4.0*
    - 15.4: Coupled Equilibria - *CC BY 4.0*
    - 15.5: Key Terms - *CC BY 4.0*
    - 15.6: Key Equations - *CC BY 4.0*
    - 15.7: Summary - *CC BY 4.0*
    - 15.8: Exercises - *CC BY 4.0*
  - 16: Thermochemistry - *CC BY 4.0*
    - 16.1: Introduction - *CC BY 4.0*
    - 16.2: Energy Basics - *CC BY 4.0*
    - 16.3: Calorimetry - *CC BY 4.0*
    - 16.4: Enthalpy - *CC BY 4.0*
    - 16.5: Key Terms - *CC BY 4.0*
    - 16.6: Key Equations - *CC BY 4.0*
    - 16.7: Summary - *CC BY 4.0*
    - 16.8: Exercises - *CC BY 4.0*
  - 17: Thermodynamics - *CC BY 4.0*
    - 17.1: Introduction - *CC BY 4.0*
    - 17.2: Spontaneity - *CC BY 4.0*
    - 17.3: Entropy - *CC BY 4.0*
    - 17.4: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
    - 17.5: Free Energy - *CC BY 4.0*
    - 17.6: Key Terms - *CC BY 4.0*

- 17.7: Key Equations - *CC BY 4.0*
- 17.8: Summary - *CC BY 4.0*
- 17.9: Exercises - *CC BY 4.0*

18: Electrochemistry - *CC BY 4.0*

- 18.1: Introduction - *CC BY 4.0*
- 18.2: Summary - *CC BY 4.0*
- 18.3: Exercises - *CC BY 4.0*
- 18.4: Review of Redox Chemistry - *CC BY 4.0*
- 18.5: Galvanic Cells - *CC BY 4.0*
- 18.6: Electrode and Cell Potentials - *CC BY 4.0*
- 18.7: Potential, Free Energy, and Equilibrium - *CC BY 4.0*
- 18.8: Batteries and Fuel Cells - *CC BY 4.0*
- 18.9: Corrosion - *CC BY 4.0*
- 18.10: Electrolysis - *CC BY 4.0*
- 18.11: Key Terms - *CC BY 4.0*
- 18.12: Key Equations - *CC BY 4.0*

19: Nuclear Chemistry - *CC BY 4.0*

- 19.1: Introduction - *CC BY 4.0*
- 19.2: Exercises - *CC BY 4.0*
- 19.3: Nuclear Structure and Stability - *CC BY 4.0*
- 19.4: Nuclear Equations - *CC BY 4.0*
- 19.5: Radioactive Decay - *CC BY 4.0*
- 19.6: Transmutation and Nuclear Energy - *CC BY 4.0*
- 19.7: Uses of Radioisotopes - *CC BY 4.0*
- 19.8: Biological Effects of Radiation - *CC BY 4.0*
- 19.9: Key Terms - *CC BY 4.0*
- 19.10: Key Equations - *CC BY 4.0*
- 19.11: Summary - *CC BY 4.0*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*

Detailed Licensing

Overview

Title: Chem 108: Textbook

Webpages: 100

All licenses found:

- CC BY 4.0: 89% (89 pages)
- Undeclared: 10% (10 pages)
- CC BY-SA 4.0: 1% (1 page)

By Page

- Chem 108: Textbook - *CC BY-SA 4.0*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 12: Kinetics - *CC BY 4.0*
    - 12.1: Introduction - *CC BY 4.0*
    - 12.2: Summary - *CC BY 4.0*
    - 12.3: Exercises - *CC BY 4.0*
    - 12.4: Chemical Reaction Rates - *CC BY 4.0*
    - 12.5: Factors Affecting Reaction Rates - *CC BY 4.0*
    - 12.6: Rate Laws - *CC BY 4.0*
    - 12.7: Integrated Rate Laws - *CC BY 4.0*
    - 12.8: Collision Theory - *CC BY 4.0*
    - 12.9: Reaction Mechanisms - *CC BY 4.0*
    - 12.10: Catalysis - *CC BY 4.0*
    - 12.11: Key Terms - *CC BY 4.0*
    - 12.12: Key Equations - *CC BY 4.0*
  - 13: Fundamental Equilibrium Concepts - *CC BY 4.0*
    - 13.1: Introduction - *CC BY 4.0*
    - 13.2: Chemical Equilibria - *CC BY 4.0*
    - 13.3: Equilibrium Constants - *CC BY 4.0*
    - 13.4: Shifting Equilibria - Le Chatelier's Principle - *CC BY 4.0*
    - 13.5: Equilibrium Calculations - *CC BY 4.0*
    - 13.6: Key Terms - *CC BY 4.0*
    - 13.7: Key Equations - *CC BY 4.0*
    - 13.8: Summary - *CC BY 4.0*
    - 13.9: Exercises - *CC BY 4.0*
  - 14: Acid-Base Equilibria - *CC BY 4.0*
    - 14.1: Introduction - *CC BY 4.0*
    - 14.2: Summary - *CC BY 4.0*
    - 14.3: Exercises - *CC BY 4.0*
    - 14.4: Brønsted-Lowry Acids and Bases - *CC BY 4.0*
    - 14.5: pH and pOH - *CC BY 4.0*
    - 14.6: Relative Strengths of Acids and Bases - *CC BY 4.0*
    - 14.7: Hydrolysis of Salt Solutions - *CC BY 4.0*
    - 14.8: Polyprotic Acids - *CC BY 4.0*
    - 14.9: Buffers - *CC BY 4.0*
    - 14.10: Acid-Base Titrations - *CC BY 4.0*
    - 14.11: Key Terms - *CC BY 4.0*
    - 14.12: Key Equations - *CC BY 4.0*
  - 15: Equilibria of Other Reaction Classes - *CC BY 4.0*
    - 15.1: Introduction - *CC BY 4.0*
    - 15.2: Precipitation and Dissolution - *CC BY 4.0*
    - 15.3: Lewis Acids and Bases - *CC BY 4.0*
    - 15.4: Coupled Equilibria - *CC BY 4.0*
    - 15.5: Key Terms - *CC BY 4.0*
    - 15.6: Key Equations - *CC BY 4.0*
    - 15.7: Summary - *CC BY 4.0*
    - 15.8: Exercises - *CC BY 4.0*
  - 16: Thermochemistry - *CC BY 4.0*
    - 16.1: Introduction - *CC BY 4.0*
    - 16.2: Energy Basics - *CC BY 4.0*
    - 16.3: Calorimetry - *CC BY 4.0*
    - 16.4: Enthalpy - *CC BY 4.0*
    - 16.5: Key Terms - *CC BY 4.0*
    - 16.6: Key Equations - *CC BY 4.0*
    - 16.7: Summary - *CC BY 4.0*
    - 16.8: Exercises - *CC BY 4.0*
  - 17: Thermodynamics - *CC BY 4.0*
    - 17.1: Introduction - *CC BY 4.0*
    - 17.2: Spontaneity - *CC BY 4.0*
    - 17.3: Entropy - *CC BY 4.0*
    - 17.4: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
    - 17.5: Free Energy - *CC BY 4.0*
    - 17.6: Key Terms - *CC BY 4.0*

- 17.7: Key Equations - *CC BY 4.0*
- 17.8: Summary - *CC BY 4.0*
- 17.9: Exercises - *CC BY 4.0*

18: Electrochemistry - *CC BY 4.0*

- 18.1: Introduction - *CC BY 4.0*
- 18.2: Summary - *CC BY 4.0*
- 18.3: Exercises - *CC BY 4.0*
- 18.4: Review of Redox Chemistry - *CC BY 4.0*
- 18.5: Galvanic Cells - *CC BY 4.0*
- 18.6: Electrode and Cell Potentials - *CC BY 4.0*
- 18.7: Potential, Free Energy, and Equilibrium - *CC BY 4.0*
- 18.8: Batteries and Fuel Cells - *CC BY 4.0*
- 18.9: Corrosion - *CC BY 4.0*
- 18.10: Electrolysis - *CC BY 4.0*
- 18.11: Key Terms - *CC BY 4.0*
- 18.12: Key Equations - *CC BY 4.0*

19: Nuclear Chemistry - *CC BY 4.0*

- 19.1: Introduction - *CC BY 4.0*
- 19.2: Exercises - *CC BY 4.0*
- 19.3: Nuclear Structure and Stability - *CC BY 4.0*
- 19.4: Nuclear Equations - *CC BY 4.0*
- 19.5: Radioactive Decay - *CC BY 4.0*
- 19.6: Transmutation and Nuclear Energy - *CC BY 4.0*
- 19.7: Uses of Radioisotopes - *CC BY 4.0*
- 19.8: Biological Effects of Radiation - *CC BY 4.0*
- 19.9: Key Terms - *CC BY 4.0*
- 19.10: Key Equations - *CC BY 4.0*
- 19.11: Summary - *CC BY 4.0*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*