CHM 118: ADVANCED GENERAL CHEMISTRY



Alexandra Strom
Smith College



CHM 118: Advanced General Chemistry (Strom)

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 and 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 06/08/2025

TABLE OF CONTENTS

Licensing

1: Radioactivity and Nuclear Chemistry

- 1.1: The Discovery of Radioactivity
- 1.2: Types of Radioactivity
- 1.3: The Valley of Stability- Predicting the Type of Radioactivity
- 1.4: Detecting Radioactivity
- 1.5: The Discovery of Fission- The Atomic Bomb and Nuclear Power
- 1.6: Converting Mass to Energy- Mass Defect and Nuclear Binding Energy
- 1.7: Nuclear Fusion - The Power of the Sun
- 1.8: Nuclear Transmutation and Transuranium Elements
- 1.9: The Effects of Radiation on Life
- 1.10: Radioactivity in Medicine and Other Applications
- 1.11: Key Terms
- 1.12: Key Equations
- 1.13: Summary
- 1.14: Exercises

2: Chemical Bonding and Molecular Geometry

- 2.1: Introduction
- 2.2: Ionic Bonding
- 2.3: Covalent Bonding
- 2.4: Lewis Symbols and Structures
- 2.5: Introduction to Formal Charges and Resonance
- 2.6: Molecular Structure and Polarity
- 2.7: Key Terms
- 2.8: Key Equations
- 2.9: Summary
- 2.10: Exercises

3: Advanced Theories of Covalent Bonding

- 3.1: Introduction
- 3.2: Molecular Orbital Theory
- 3.3: Valence Bond Theory
- 3.4: Hybrid Atomic Orbitals
- 3.5: Multiple Bonds formed between Hybridized Atoms
- 3.6: Resonance
- 3.7: Rules for Resonance Forms
- 3.8: Resonance Effects on Hybridization and Bonding
- 3.9: Hybridized Orbital Energy Diagrams
- 3.10: Key Terms
- 3.11: Summary
- 3.12: Exercises

4: Thermochemistry

- 4.1: Introduction
- 4.2: Energy Basics
- 4.3: Calorimetry
- 4.4: Enthalpy
- 4.5: Strengths of Ionic and Covalent Bonds
- 4.6: Key Terms
- 4.7: Key Equations
- 4.8: Summary
- 4.9: Exercises

5: Thermodynamics

- 5.1: Introduction
- 5.2: Spontaneity
- 5.3: Entropy
- 5.4: The Second and Third Laws of Thermodynamics
- 5.5: Free Energy
- 5.6: Key Terms
- 5.7: Key Equations
- 5.8: Summary
- 5.9: Exercises

6: Fundamental Equilibrium Concepts

- 6.1: Introduction
- 6.2: Chemical Equilibria
- 6.3: Equilibrium Constants
- 6.4: Shifting Equilibria - Le Chatelier’s Principle
- 6.5: Equilibrium Calculations
- 6.6: Free Energy Equilibria
- 6.7: Key Terms
- 6.8: Key Equations
- 6.9: Summary
- 6.10: Exercises

7: Acid-Base Equilibria

- 7.1: Introduction
- 7.2: Brønsted-Lowry Acids and Bases
- 7.3: pH and pOH
- 7.4: Relative Strengths of Acids and Bases
- 7.5: Hydrolysis of Salt
- 7.6: Polyprotic Acids
- 7.7: Buffers
- 7.8: Acid-Base Titrations
- 7.9: Key Terms
- 7.10: Key Equations
- 7.11: Summary
- 7.12: Exercises

8: Kinetics

- 8.1: Introduction
- 8.2: Chemical Reaction Rates
- 8.3: Factors Affecting Reaction Rates
- 8.4: Rate Laws
- 8.5: Integrated Rate Laws
- 8.6: Collision Theory
- 8.7: Reaction Mechanisms
- 8.8: Catalysis
- 8.9: Key Terms
- 8.10: Key Equations
- 8.11: Summary
- 8.12: Exercises

9: Electrochemistry

- 9.1: Introduction
- 9.2: Review of Redox Chemistry
- 9.3: Galvanic Cells
- 9.4: Electrode and Cell Potentials
- 9.5: Potential, Free Energy, and Equilibrium
- 9.6: Batteries and Fuel Cells
- 9.7: Corrosion
- 9.8: Electrolysis
- 9.9: Key Terms
- 9.10: Key Equations
- 9.11: Summary
- 9.12: Exercises

10: Appendices

- 10.1: Appendix A- The Periodic Table
- 10.2: Appendix B- Essential Mathematics
- 10.3: Appendix C- Units and Conversion Factors
- 10.4: Appendix D- Fundamental Physical Constants
- 10.5: Appendix E- Water Properties
- 10.6: Appendix F- Composition of Commercial Acids and Bases
- 10.7: Appendix G- Standard Thermodynamic Properties for Selected Substances
- 10.8: Appendix H- Ionization Constants of Weak Acids
- 10.9: Appendix I- Ionization Constants of Weak Bases
- 10.10: Appendix J- Solubility Products
- 10.11: Appendix K- Formation Constants for Complex Ions
- 10.12: Appendix L- Standard Electrode (Half-Cell) Potentials
- 10.13: Appendix M- Half-Lives for Several Radioactive Isotopes
- 10.14: Answer Keys
  - 10.14.1: Chapter 1 - Radioactivity and Nuclear Chemistry
  - 10.14.2: Chapter 2 - Chemical Bonding and Molecular Geometry
  - 10.14.3: Chapter 3 - Advanced Theories of Covalent Bonding
  - 10.14.4: Chapter 4 - Thermochemistry
  - 10.14.5: Chapter 5 - Thermodynamics
  - 10.14.6: Chapter 6 - Fundamental Equilibrium Concepts
  - 10.14.7: Chapter 7 - Acid-Base Equilibria

- 10.14.8: Chapter 8 - Kinetics
- 10.14.9: Chapter 9 - Electrochemistry

Index

Glossary

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Radioactivity and Nuclear Chemistry

Template:HideTOC

1.1: The Discovery of Radioactivity
1.2: Types of Radioactivity
1.3: The Valley of Stability- Predicting the Type of Radioactivity
1.4: Detecting Radioactivity
1.5: The Discovery of Fission- The Atomic Bomb and Nuclear Power
1.6: Converting Mass to Energy- Mass Defect and Nuclear Binding Energy
1.7: Nuclear Fusion - The Power of the Sun
1.8: Nuclear Transmutation and Transuranium Elements
1.9: The Effects of Radiation on Life
1.10: Radioactivity in Medicine and Other Applications
1.11: Key Terms
1.12: Key Equations
1.13: Summary
1.14: Exercises

1: Radioactivity and Nuclear Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.1: The Discovery of Radioactivity

Learning Objectives

- List the most common emissions from naturally radioactive nuclei.
- Compare the energy released per gram of matter in nuclear reactions to that in chemical reactions.
- Express the relationship between nuclear stability and the nuclei's binding energy per nucleon ratio.

No one could have known in the 1800's that the discovery of the fascinating science and art form of photography would eventually lead to the splitting of the atom. The basis of photography is the fact that visible light causes certain chemical reactions. If the chemicals are spread thinly on a surface but protected from light by a covering, no reaction occurs. When the covering is removed, however, light acting on the chemicals causes them to darken. With millions of cameras in use today, we do not think of it as a strange phenomenon—but at the time of its discovery, photography was a strange and wonderful thing.

Even stranger was the discovery by Wilhelm Roentgen—that radiation other than visible light could expose photographic film. He found that film wrapped in dark paper would react when x-rays went through the paper and struck the film.



Figure 1.1.1: Image of Becquerel's photographic plate, which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).

When Henri Becquerel heard about Roentgen's discovery, he wondered if his fluorescent minerals would give the same x-rays. Becquerel placed some of his rock crystals on top of a well-covered photographic plate and sat them in the sunlight. The sunlight made the crystals glow with a bright fluorescent light, but when Becquerel developed the film he was very disappointed. He found that only one of his minerals, a uranium salt, had fogged the photographic plate. He decided to try again, and this time, to leave them out in the sun for a longer period of time. Fortunately, the weather didn't cooperate, and Becquerel had to leave the crystals and film stored in a drawer for several cloudy days. Before continuing his experiments, Becquerel decided to check one of the photographic plates to make sure the chemicals were still good. To his amazement, he found that the plate had been exposed in spots where it had been near the uranium containing rocks, and some of these rocks had not been exposed to sunlight at all. In later experiments, Becquerel confirmed that the radiation from the uranium had no connection with light or fluorescence, but the amount of radiation was directly proportional to the concentration of uranium in the rock. Becquerel had discovered **radioactivity**.

The Curies and Radium

One of Becquerel's assistants, a young Polish scientist named Maria Sklowdowska (to become Marie Curie after she married Pierre Curie), became interested in the phenomenon of radioactivity. With her husband, she decided to find out if chemicals other than uranium were radioactive. The Austrian government was happy to send the Curies a ton of pitchblende from the mining region of Joachimstahl, because it was waste material that had to be disposed of anyway. The Curies wanted the pitchblende because it was the residue of uranium mining. From the ton of pitchblende, the Curies separated $0.10\ \text{g}$ of a previously unknown element, radium, in the form of the compound radium chloride. This radium was many times more radioactive than uranium.

By 1902, the world was aware of a new phenomenon called radioactivity and of new elements which exhibited natural radioactivity. For this work, Becquerel and the Curies shared the 1903 Nobel Prize and for subsequent work; Marie Cure received a second Nobel Prize in 1911. She is the only person ever to receive two Nobel Prizes in science.

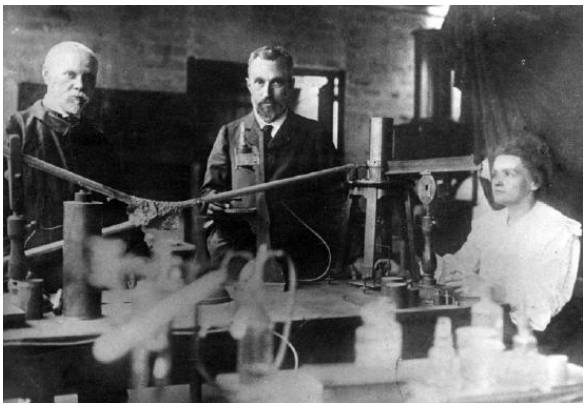


Figure 1.1.2: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

Further experiments provided information about the characteristics of the penetrating emissions from radioactive substances. It was soon discovered that there were three common types of radioactive emissions. Some of the radiation could pass easily through aluminum foil while some of the radiation was stopped by the foil. Some of the radiation could even pass through foil up to a centimeter thick. The three basic types of radiation were named alpha, beta, and gamma radiation. The actual composition of the three types of radiation was still not known.

Eventually, scientists were able to demonstrate experimentally that the alpha particle, α, was a helium nucleus (a particle containing two protons and two neutrons), a beta particle, β, was a high speed electron, and gamma rays, γ, were a very high energy form of light (even higher energy than x-rays).

Unstable Nuclei May Disintegrate

A nucleus (with one exception, hydrogen-1) consists of some number of protons and neutrons pulled together in an extremely tiny volume. Since protons are positively charged and like charges repel, it is clear that protons cannot remain together in the nucleus unless there is a powerful force holding them there. The force which holds the nucleus together is generated by **nuclear binding energy**.

A nucleus with a large amount of binding energy per nucleon (proton or neutron) will be held together tightly and is referred to as stable. These nuclei do not break apart. When there is too little binding energy per nucleon, the nucleus will be less stable and may disintegrate (come apart). Such disintegration is referred to as **natural radioactivity**. It is also possible for scientists to smash nuclear particles together and cause nuclear reactions between normally stable nuclei. This disintegration is referred to as **artificial radioactivity**. None of the elements above #92 on the periodic table occur on earth naturally—they are all products of artificial (manmade) radioactivity.

When nuclei come apart, they come apart violently accompanied by a tremendous release of energy in the form of heat, light, and radiation. This energy comes from some of the nuclear binding energy. In nuclear changes, the energy involved comes from the nuclear binding energy. However, in chemical reactions, the energy comes from electrons moving energy levels. A typical nuclear change (such as fission) may involve millions of times more energy per atom changing compared to a chemical change (such as burning)!

Summary

- Henri Becquerel, Marie Curie, and Pierre Curie shared the discovery of radioactivity.

Contributions & Attributions

- Wikibooks
-

1.1: The Discovery of Radioactivity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.2: The Discovery of Radioactivity** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

1.2: Types of Radioactivity

Learning Objectives

- Write and balance nuclear equations
- To know the different kinds of radioactive decay.
- To balance a nuclear reaction.

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of ${}^{1}_{1}\text{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation:

$$ {}^{\text{A}}_{\text{Z}}\text{X} \tag{1.2.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, ${}^{14}_{6}\text{C}$ is called "carbon-14."

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{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/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger).

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.

Nuclear Equations

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that ${}^{17}_{8}\text{O}$ is a product of the nuclear reaction of ${}^{14}_{7}\text{N}$ and ${}^{4}_{2}\text{He}$ if we knew that a proton, ${}^{1}_{1}\text{H}$, was one of the two products. Example 1.2.1 shows how we can identify a nuclide by balancing the nuclear reaction.

Example 1.2.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 $\left({}^{25}_{12}\text{Mg}\right)$ produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\text{Mg} + ^{4}_{2}\text{He} \rightarrow ^{1}_{1}\text{H} + ^{\text{A}}_{\text{Z}}\text{X}$$

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:

$$25 + 4 = \text{A} + 1$$

so

$$\text{A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \text{Z} + 1$$

so

$$\text{Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\text{Al}$.

? Exercise 1.2.1

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

$$^{125}_{53}\text{I} + ^{0}_{-1}\text{e} \rightarrow ^{125}_{52}\text{Te}$$

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> *Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.*

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the $^{A}_{Z}\text{X}$ notation for nuclides to include radioactive emissions. Table 1.2.1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table 1.2.1: Nuclear Decay Emissions and Their Symbols

Identity	Symbol	Charge	Mass (amu)
helium nucleus	${}^{4}_{2}\alpha$	+2	4.001506
electron	${}^{0}_{-1}\beta$ or β^{-}	−1	0.000549
photon	${}^{0}_{0}\gamma$	—	—
neutron	${}^{1}_{0}\mathrm{n}$	0	1.008665
proton	${}^{1}_{1}\mathrm{p}$	+1	1.007276
positron	${}^{0}_{+1}\beta$ or β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = −1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to e^{-}, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to β^{-}, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 1.2.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

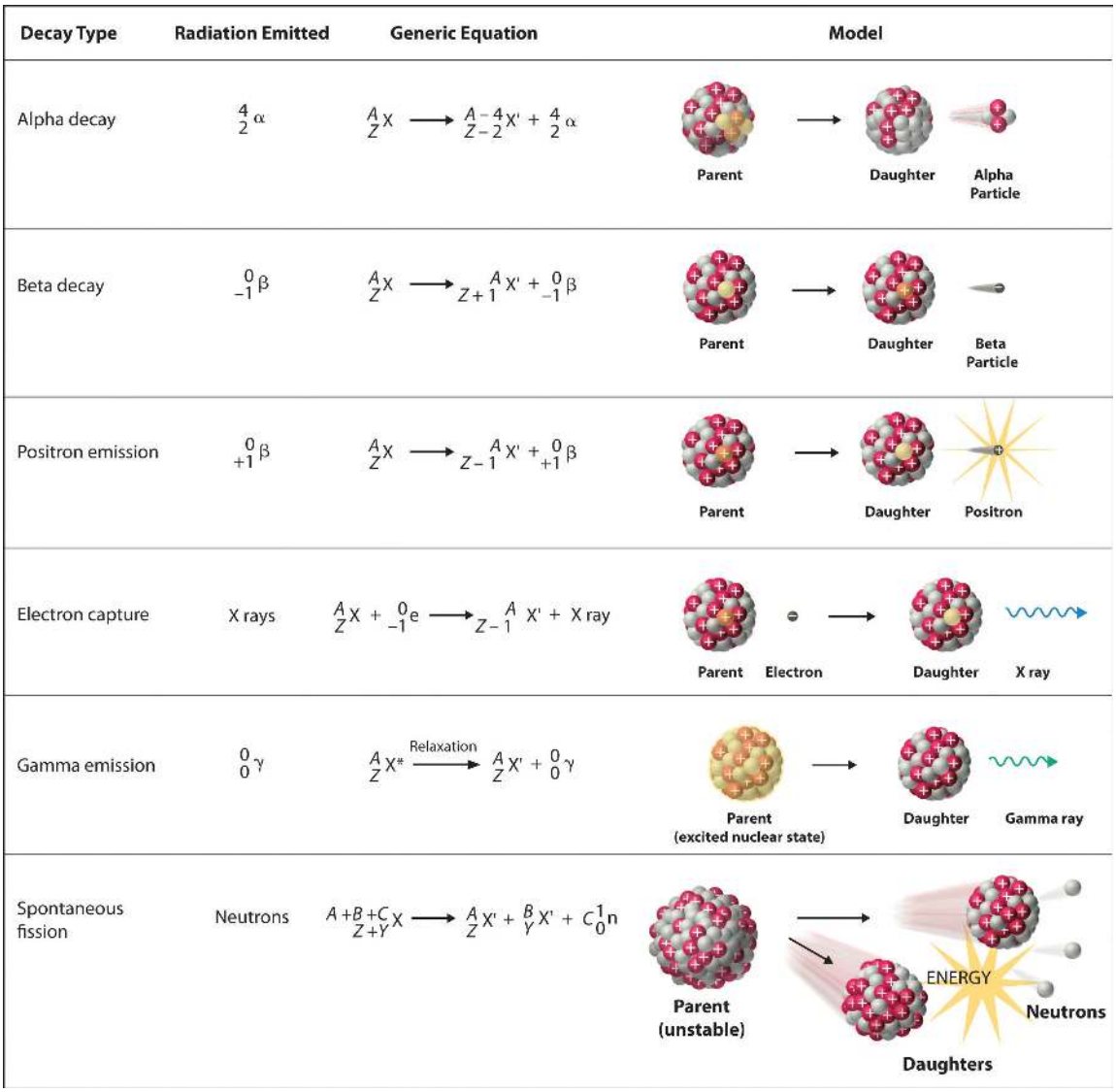


Figure 1.2.1: Common Modes of Nuclear Decay

The different types of decay are alpha, beta, positron emission, electron capture, gamma emission, and spontaneous fission.

Alpha α Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\ \text{particle}}}{{}^{4}_{2}\alpha} \tag{1.2.2}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha \tag{1.2.3}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

> *Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.*

Beta β^- Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{1.2.4}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{1.2.5}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron β^+ Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{1.2.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta^{+}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n} \tag{1.2.7}$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} + \underset{\text{electron}}{{}^{0}_{-1}\text{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \text{x-ray}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$^{55}_{26}\text{Fe} \xrightarrow{\text{EC}} {}^{55}_{25}\text{Mn} + \text{x-ray}$$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$^{55}_{26}\text{Fe} + {}^{0}_{-1}\text{e} \rightarrow {}^{55}_{25}\text{Mn} + \text{x-ray}$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma γ Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\text{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{{}^{234}_{90}\text{Th}^*} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\text{Th}^* \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma$$

or more generally,

$$^{A}_{Z}\text{X}^* \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4{}^{1}_{0}\text{n}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

✔ Example 1.2.2

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\text{S}$

b. the decay of $^{201}_{80}\text{Hg}$ by electron capture
c. the decay of $^{30}_{15}\text{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as $^{A}_{Z}\text{X}$:

$$^{35}_{16}\text{S} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{-1}\beta$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of *A* = 35 − 0 = 35 and an atomic number of *Z* = 16 − (−1) = 17. The element with *Z* = 17 is chlorine, so the balanced nuclear equation is as follows:

$$^{35}_{16}\text{S} \rightarrow {}^{35}_{17}\text{Cl} + {}^{0}_{-1}\beta$$

b.

A We know the identities of both reactants: $^{201}_{80}\text{Hg}$ and an inner electron, $^{0}_{-1}\text{e}$. The reaction is as follows:

$$^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{A}_{Z}\text{X}$$

B Both protons and neutrons are conserved, so the mass number of the product must be *A* = 201 + 0 = 201, and the atomic number of the product must be *Z* = 80 + (−1) = 79, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{201}_{79}\text{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\text{P} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{+1}\beta$$

B The mass number of the second product is *A* = 30 − 0 = 30, and its atomic number is *Z* = 15 − 1 = 14, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\text{P} \rightarrow {}^{30}_{14}\text{Si} + {}^{0}_{+1}\beta$$

? Exercise 1.2.2

Write a balanced nuclear equation to describe each reaction.

a. $^{11}_{6}\text{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from $^{185}_{74}\text{W}$

Answer a

$$^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta$$

Answer d

$$^{99}_{42}\text{Mo} \rightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\beta$$

Answer c

$^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

Example 1.2.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\mathrm{Ti}$
b. $^{242}_{94}\mathrm{Pu}$
c. $^{12}_{5}\mathrm{B}$
d. $^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 1.2.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

Answer a

beta decay

Answer d

positron emission or electron capture

Answer c

alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases Z by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 1.2.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of "only" 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

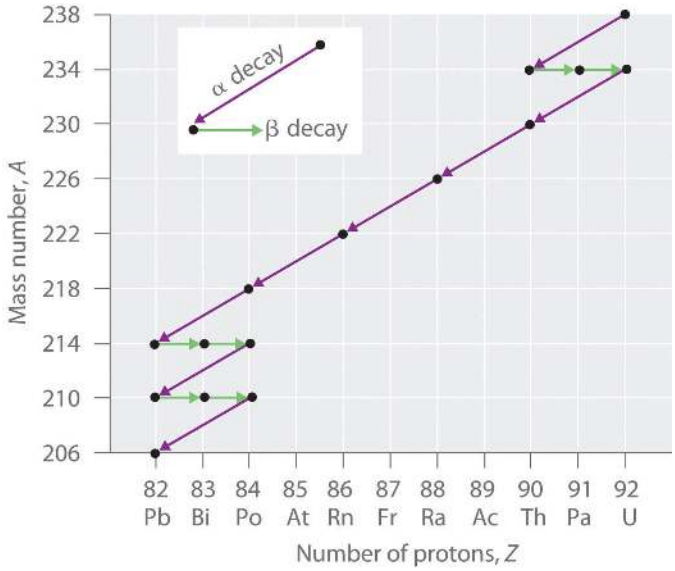


Figure 1.2.2 A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Graph of mass number against number of protons. The purple lines are alpha decay which are linear while the green lines are beta decay and are horizontal and parallel to the x axis.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p}$$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{1.2.8}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 1.2.3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{1.2.9}$$

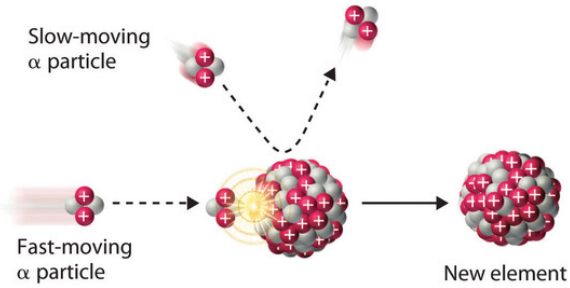


Figure 1.2.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

Example 1.2.4

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (Z = 13) will be converted to phosphorus (Z = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}\mathrm{P}$.

B The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n}$$

? Exercise 1.2.4

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei ($^{2}_{1}\mathrm{H}$) produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

Answer

neutron, $^{1}_{0}\mathrm{n}$; $^{96}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{97}_{43}\mathrm{Tc} + {}^{1}_{0}\mathrm{n}$:

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 1.2.4:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{1.2.10}$$

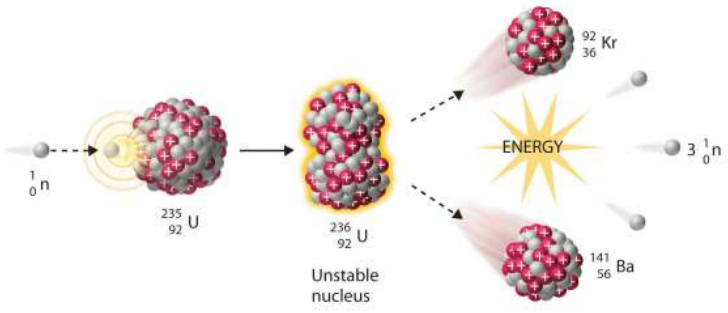


Figure 1.2.4 Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 1.2.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 1.2.5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

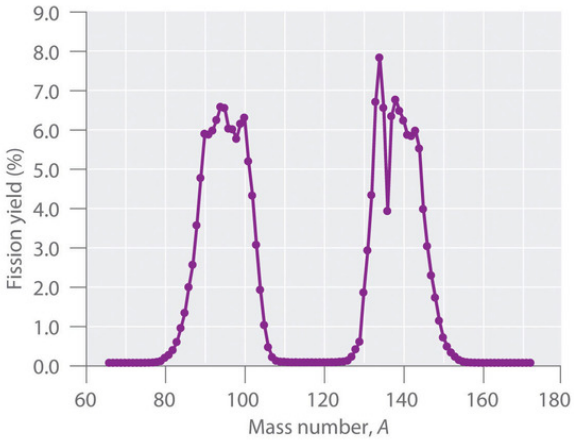


Figure 1.2.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for ^{235}U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 1.2.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 1.2.2: Some Reactions Used to Synthesize Transuranium Elements

$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{1}_{1}\mathrm{p} + {}^{1}_{0}\mathrm{n}$
$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\mathrm{Bk} + {}^{1}_{1}\mathrm{p} + 2{}^{1}_{0}\mathrm{n}$
$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4{}^{1}_{0}\mathrm{n}$
$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{256}_{103}\mathrm{Lr} + 6{}^{1}_{0}\mathrm{n}$

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 1.2.6), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

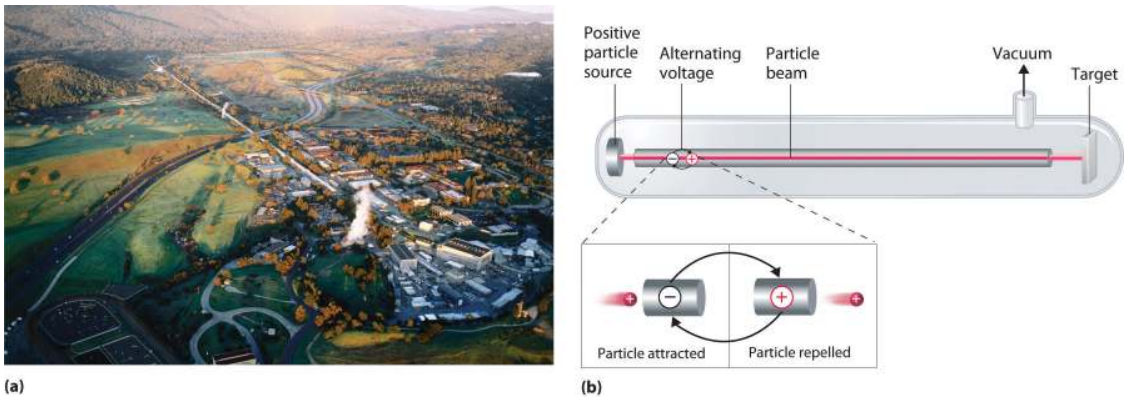


Figure 1.2.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

Summary and Key Takeaway

- Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, ${}^{4}_{2}\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

Key Equations

alpha decay

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha $$

beta decay

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta $$

positron emission

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta $$

electron capture

$$ {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray} $$

gamma emission

$$ {}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma $$

1.2: Types of Radioactivity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.1: Radioactivity** is licensed CC BY-NC-SA 3.0.

1.3: The Valley of Stability- Predicting the Type of Radioactivity

Learning Objectives

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or decay, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

Each element can be represented by the notation ${}^{A}_{Z}\mathrm{X}$, where *A*, the mass number, is the sum of the number of protons and the number of neutrons, and *Z*, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called **nucleons**, and an atom with a particular number of protons and neutrons is called a **nuclide**. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

stable isotopes of oxygen represented in different ways

${}^{A}_{Z}\mathrm{X}$	${}^{16}_{8}\mathrm{O}$	${}^{17}_{8}\mathrm{O}$	${}^{18}_{8}\mathrm{O}$
${}^{A}\mathrm{X}$	${}^{16}\mathrm{O}$	${}^{17}\mathrm{O}$	${}^{18}\mathrm{O}$
element-A:	oxygen-16	oxygen-17	oxygen-18

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17. Any nucleus that is unstable and decays spontaneously is said to be **radioactive**, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called **radioisotopes**.

Nuclear Stability

The nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the **strong nuclear force**, an extremely powerful but very short-range attractive force between nucleons (Figure 1.3.1). All stable nuclei except the hydrogen-1 nucleus (${}^{1}\mathrm{H}$) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

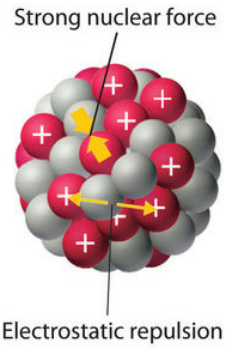


Figure 1.3.1: Competing Interactions within the Atomic Nucleus. Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 1.3.2. The stable isotopes form a "peninsula of stability" in a "sea of instability." Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $^{4}_{2}He$, $^{10}_{5}B$, and $^{40}_{20}Ca$). All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with Z > 83 are unstable and radioactive.

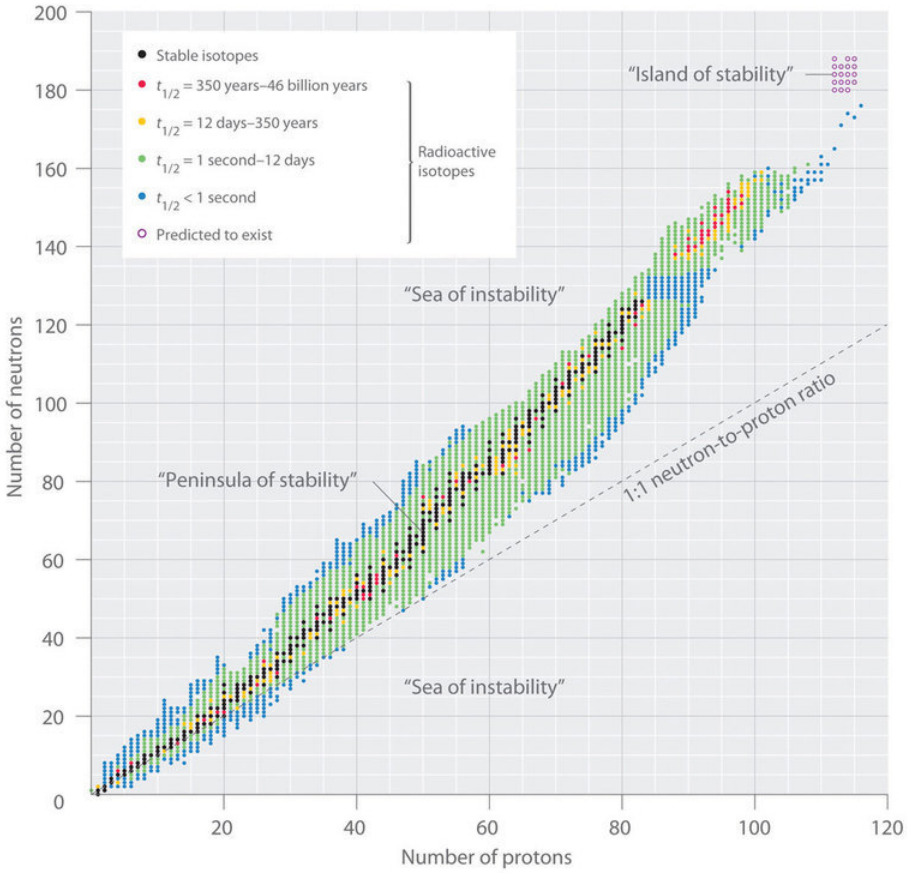


Figure 1.3.2: The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio. In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized. Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.

Graph of number or neutrons against the number or protons. The graph is divided into sections of "sea of instability", "peninsula of stability", "sea of instability" and "island of stability"

As shown in Figure 1.3.3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be “doubly magic” and are even more stable. Examples of elements with doubly magic nuclei are $^{4}_{2}\text{He}$, with 2 protons and 2 neutrons, and $^{208}_{82}\text{Pb}$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

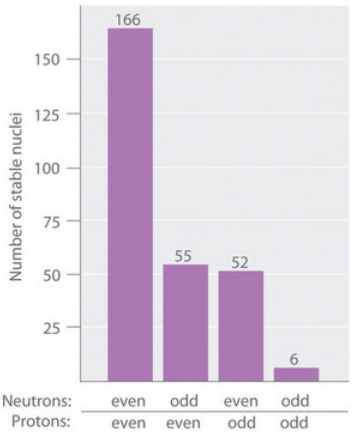


Figure 1.3.3: The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.

> *Most stable nuclei contain **even** numbers of both neutrons and protons*

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 1.3.2, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Origin of the Magic Numbers

Multiple models have been formulated to explain the origin of the magic numbers and two popular ones are the Nuclear Shell Model and the Liquid Drop Model. Unfortuneatly, both require advanced quantum mechanics to fully understand and are beyond the scope of this text.

Example 1.3.1

Classify each nuclide as stable or radioactive.

a. $^{30}_{15}\mathrm{P}$
b. $^{98}_{43}\mathrm{Tc}$
c. tin-118
d. $^{239}_{94}\mathrm{Pu}$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

a. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 1.3.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $^{30}_{15}\mathrm{P}$ is predicted to be radioactive, and it is.

b. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}\mathrm{Tc}$ near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest that $^{98}_{43}\mathrm{Tc}$ might be stable. However, $^{98}_{43}\mathrm{Tc}$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}\mathrm{Tc}$ is predicted to be radioactive, and it is.

c. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an even number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $^{118}_{50}\mathrm{Sn}$should be particularly stable.

d. This nuclide has an atomic number of 94. Because all nuclei with Z > 83 are unstable, $^{239}_{94}\mathrm{Pu}$ must be radioactive.

? Exercise 1.3.1

Classify each nuclide as stable or radioactive.

a. $^{232}_{90}\mathrm{Th}$
b. $^{40}_{20}\mathrm{Ca}$
c. $^{15}_{8}\mathrm{O}$
d. $^{139}_{57}\mathrm{La}$

Answer a

radioactive

Answer b

stable

Answer c

radioactive

Answer d

stable

Superheavy Elements

In addition to the “peninsula of stability” there is a small “island of stability” that is predicted to exist in the upper right corner. This island corresponds to the **superheavy elements**, with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with Z = 114 and Z = 116 have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an “eternity” by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with A = 292 that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with Z = 122. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

1.3: The Valley of Stability- Predicting the Type of Radioactivity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.2: Patterns of Nuclear Stability** is licensed CC BY-NC-SA 3.0.

1.4: Detecting Radioactivity

Learning Objectives

- Understand how the Geiger counter can be used to quantify the rate of ionization radiation.

When alpha, beta or gamma particles collide with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. Alpha, beta and gamma radiation are broadly referred to as **ionizing radiation**. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this in order to detect these particles. In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry. Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter. A simple schematic of a Geiger counter is shown in Figure 1.4.1.

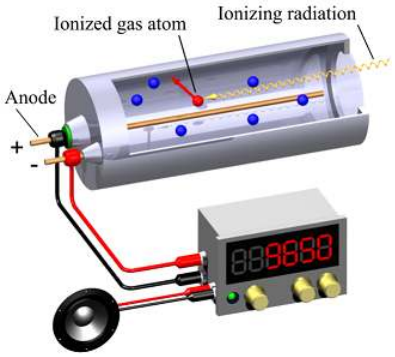


Figure 1.4.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia(opens in new window)).

Although scientists were not aware at the time of the Geiger counter's invention, all of us are subjected to a certain amount of radiation every day. This radiation is called **background radiation** and comes from a variety of natural and artificial radiation sources. Approximately 82% of background radiation comes from natural sources. These natural sources include:

1. Sources in the earth—including naturally occurring radioactive elements—which are incorporated in building materials, and also in the human body.
2. Sources from space in the form of cosmic rays.
3. Sources in the atmosphere, such as radioactive radon gas released from the earth; and radioactive atoms like carbon-14, produced in the atmosphere by bombardment from high-energy cosmic rays.

Measuring Radiation Exposure

1.4: Detecting Radioactivity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.4: Detecting Radioactivity** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

1.5: The Discovery of Fission- The Atomic Bomb and Nuclear Power

Learning Objectives

- Explain nuclear fission
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for 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. 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 1.5.1.

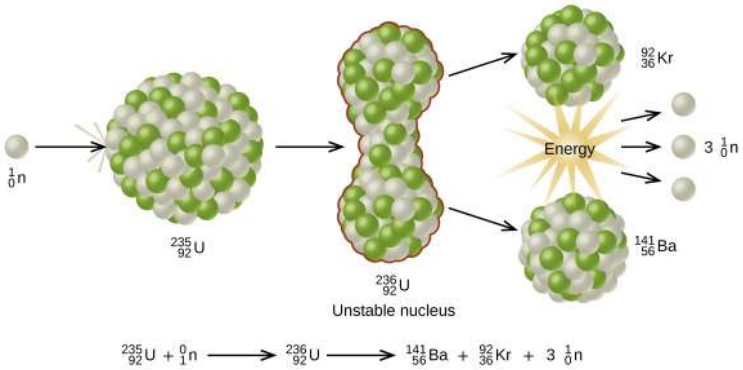


Figure 1.5.1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount 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 1.5.2. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

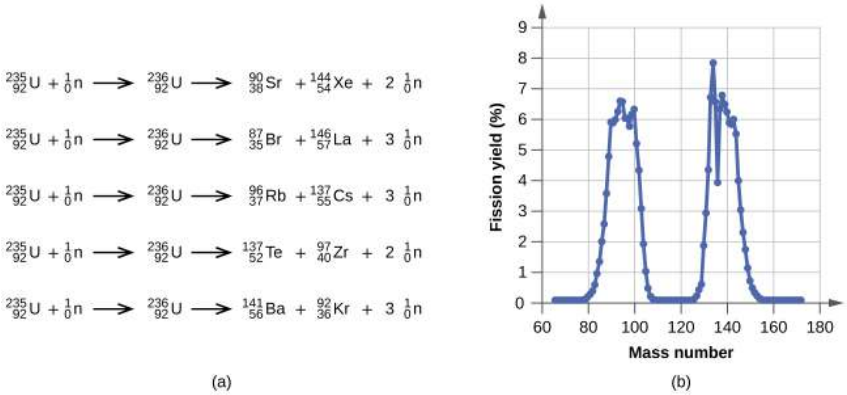


Figure 1.5.2: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

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 (Figure 1.5.3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

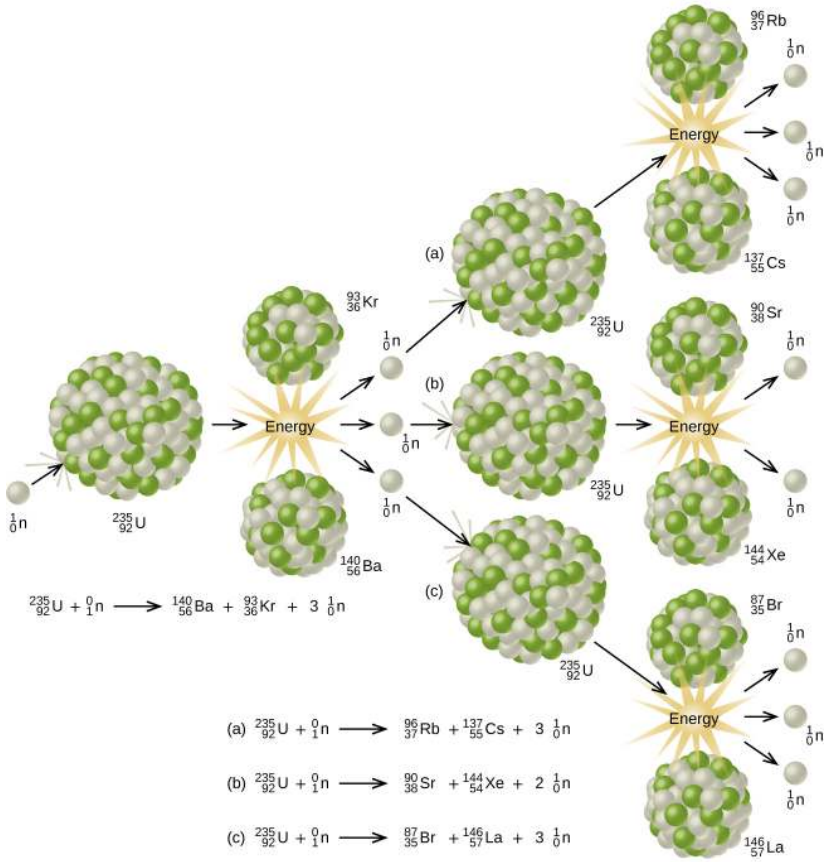


Figure 1.5.3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

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 1.5.4).

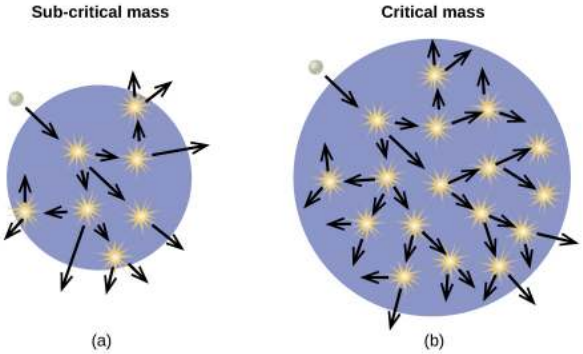


Figure 1.5.4: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 1.5.5) contains several pounds of fissionable material, $^{235}_{92}U$ or $^{239}_{94}Pu$, 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.

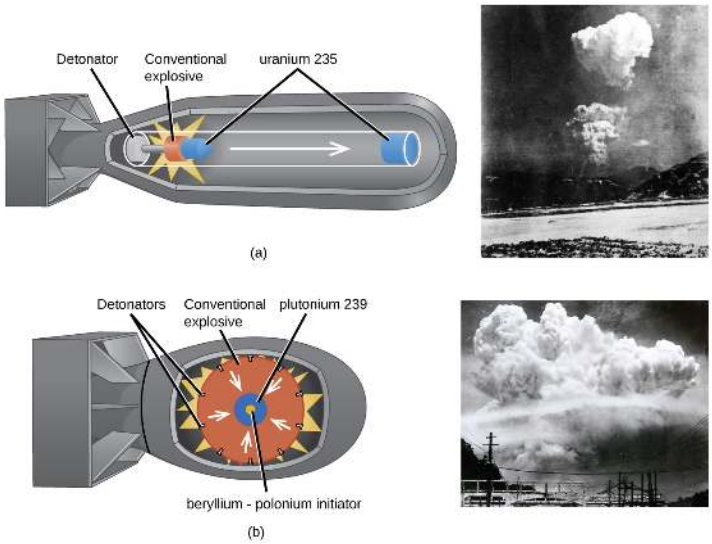


Figure 1.5.5: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 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 1.5.6). 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.

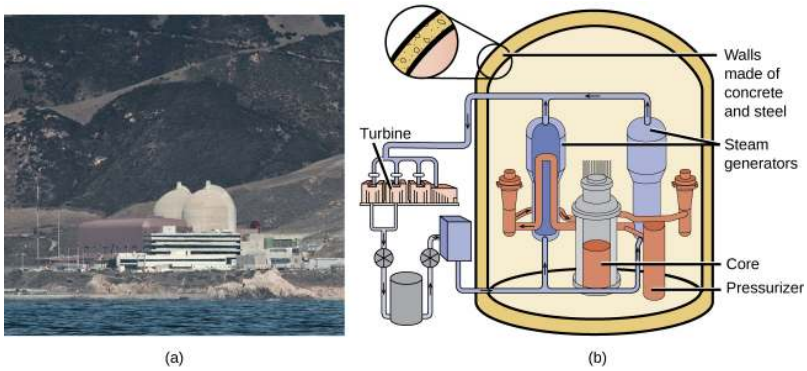


Figure 1.5.6: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is 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 (Figure 1.5.4). 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 $\left({}^{2}_{1}H_2O\right)$ 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 1.5.8) 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:

$$^{10}_{5}B + {}^{1}_{0}n \longrightarrow {}^{7}_{3}Li + {}^{4}_{2}He \tag{1.5.1}$$

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.

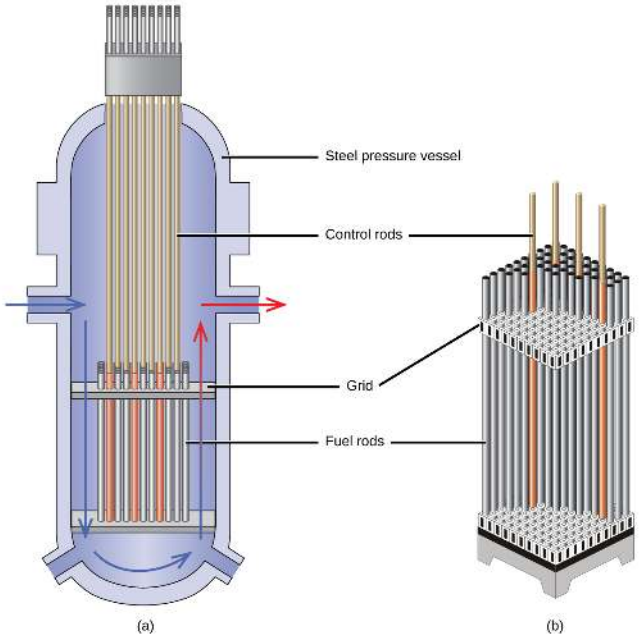


Figure 1.5.7: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, glossary.periodni.com/glossar...en=control+rod)

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.



Video* 1.5.1*: *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.

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:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g) \tag{1.5.2}$$

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 1.5.8).

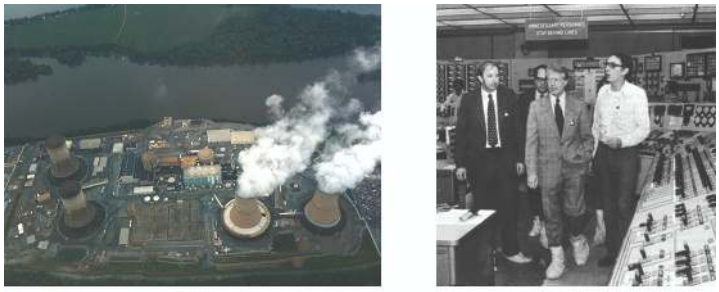


Figure 1.5.8: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control 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 1.5.10).



Figure 1.5.9: (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.

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

This page titled 1.5: The Discovery of Fission- The Atomic Bomb and Nuclear Power is shared under a CC BY license and was authored, remixed, and/or curated by OpenStax.

- **25.8: Nuclear Fission** by OpenStax is licensed CC BY-NC-SA 4.0.

1.6: Converting Mass to Energy- Mass Defect and Nuclear Binding Energy

Learning Objectives

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

The relationship between mass (m) and energy (E) is expressed in the following equation:

$$E = mc^2 \tag{1.6.1}$$

where

- c is the speed of light ($2.998 \times 10^8\ m/s$), and
- E and m are expressed in units of joules and kilograms, respectively.

Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 1.6.1, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5\ \mathrm{kJ/mol} \tag{1.6.2}$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. When a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, ΔE ≈ ΔH. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)c^2 \tag{1.6.3}$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \tag{1.6.4}$$

Because 1 J = 1 (kg•m^2)/s^2, the change in mass is as follows:

$$\Delta m = \frac{-393.5\ \mathrm{kJ/mol}}{(2.998 \times 10^8\ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5\ (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8\ \mathrm{m/s})^2} = -4.38 \times 10^{-12}\ \mathrm{kg/mol} \tag{1.6.5}$$

This is a mass change of about 3.6 × 10^{-10} g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ^{14}C to ^{14}N and an electron (a β particle), there is a much larger change in mass:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{1.6.6}$$

We can use the experimentally measured masses of subatomic particles (Table 1.2.1) and common isotopes given in Table 1.6.1 to calculate the change in mass directly. The reaction involves the conversion of a neutral ^{14}C atom to a positively charged ^{14}N ion (with six, not seven, electrons) and a negatively charged β particle (an electron).

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{1.6.7}$$

$$= [(14.003074\ \text{amu} - 0.000549\ \text{amu}) + 0.000549\ \text{amu}] - 14.003242\ \text{amu} = -0.000168\ \text{amu} \tag{1.6.8}$$

The mass of the products is identical to the mass of a neutral ^{14}N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral ^{14}N atom (14.003074 amu) and the mass of a ^{14}C atom (14.003242 amu):

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{1.6.9}$$

$$= 14.003074\ \text{amu} - 14.003242\ \text{amu} = -0.000168\ \text{amu} \tag{1.6.10}$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of ^{14}C is −0.000168 g = -1.68×10^{-4} g = -1.68×10^{-7} kg. Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. This example highlights the importance of accounting for charges when calculating the mass defect. The energy change is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7}\ \text{kg})(2.998 \times 10^{8}\ \text{m/s})^2 \tag{1.6.11}$$

$$= -1.51 \times 10^{10}(\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10}\ \text{J} = -1.51 \times 10^{7}\ \text{kJ} \tag{1.6.12}$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

$$(-1.68 \times 10^{-4}\ \text{amu})\left(\frac{931\ \text{MeV}}{\text{amu}}\right) = -0.156\ \text{MeV} = -156\ \text{keV}$$

Table 1.6.1: Experimentally Measured Masses of Selected Isotopes

Isotope	Mass (amu)	Isotope	Mass (amu)	Isotope	Mass (amu)
^{1}H	1.007825	^{90}Sr	89.907738	^{222}Rn	222.017578
^{2}H	2.014102	^{90}Rb	89.914802	^{226}Ra	226.025410
^{3}H	3.016049	^{92}Kr	91.926156	^{227}Ra	227.029178
^{3}He	3.016029	^{141}Ba	140.914411	^{228}Ac	228.031021
^{4}He	4.002603	^{143}Xe	142.935110	^{230}Th	230.033134
^{6}Li	6.015123	^{144}Cs	143.932077	^{233}U	233.039635
^{7}Li	7.016005	^{167}Os	166.971550	^{234}Th	234.043601
^{9}Be	9.012182	^{171}Pt	170.981240	^{234}Pa	234.043308
^{8}B	8.024607	^{194}Hg	193.965439	^{235}U	235.043930
^{10}B	10.012937	^{194}Tl	193.971200	^{238}Pa	238.054500
^{11}B	11.009305	^{199}Pb	198.972917	^{238}U	238.050788
^{12}C	12	^{199}Bi	198.977672	^{239}Pu	239.052163

^{13}C	13.003355	^{206}Pb	205.974465	^{245}Pu	245.067747
^{14}C	14.003242	^{207}Pb	206.975897		
^{14}N	14.003074	^{208}Pb	207.976652		
^{16}O	15.994915	^{208}Bi	207.979742		
^{40}K	39.963998	^{208}Po	207.981246		
^{52}Cr	51.940508	^{209}Fr	208.99592		
^{56}Fe	55.934938	^{210}Po	209.982874		
^{58}Ni	57.935343	^{212}At	211.990745		
^{59}Co	58.933195	^{214}Pb	213.999797		
^{60}Co	59.933817	^{214}Bi	213.998712		
^{60}Ni	59.930786	^{216}Fr	216.003198		

Example 1.6.1

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of ^{238}U to ^{234}Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values in Table 1.2.1 and Table 1.6.1 to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 1.6.4 to calculate the change in energy in joules per mole.

C Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

Solution

A Using particle and isotope masses from Table 1.2.1, we can calculate the change in mass as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } ^{234}\text{Th} + \text{mass } {}^{4}_{2}\text{He}) - \text{mass } ^{238}\text{U} \quad (1.6.13)$$

$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \quad (1.6.14)$$

B Thus the change in mass for 1 mol of ^{238}U is −0.004584 g or -4.584×10^{-6} kg. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6} \text{ kg})(2.998 \times 10^{8} \text{ m/s})^2 = -4.120 \times 10^{11} \text{ J/mol}$$

C The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.584 \times 10^{-3} \text{ amu} \times \frac{931 \text{ MeV}}{\text{amu}} \times \frac{1 \times 10^{6} \text{ eV}}{1 \text{ MeV}} = -4.27 \times 10^{6} \text{ eV/atom}$$

Exercise 1.6.1

Calculate the changes in mass (in atomic mass units) and energy (in kilojoules per mole and kiloelectronvolts per atom) that accompany the radioactive decay of tritium (^{3}H) to ^{3}He and a β particle.

Answer

$\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^{6}$ kJ/mol = −19 keV/atom

Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 (^{1}H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium (^{2}H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

$$m_{^2\mathrm{H}} = m_{\text{neutron}} + m_{\text{proton}} + m_{\text{electron}} \tag{1.6.15}$$

$$= 1.008665\ \text{amu} + 1.007276\ \text{amu} + 0.000549\ \text{amu} = 2.016490\ \text{amu} \tag{1.6.16}$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 1.6.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

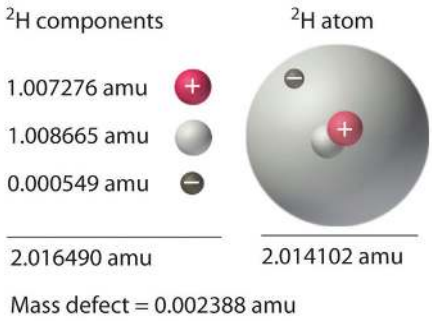


Figure 1.6.1: Nuclear Binding Energy in Deuterium. The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 1.6.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

> *Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.*

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 1.6.2, the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

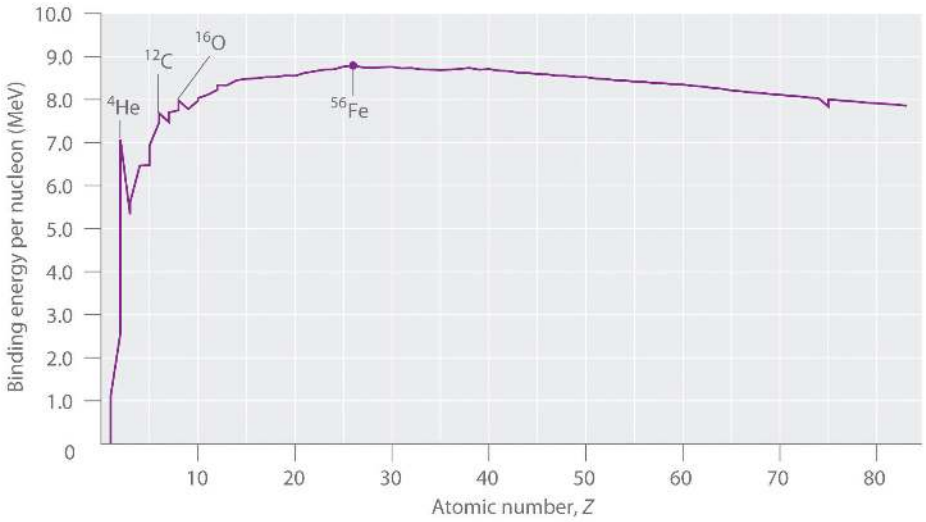


Figure 1.6.2: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in Figure 1.6.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 1.6.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

> *Heavier nuclei spontaneously undergo nuclear reactions that decrease their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that increase their atomic number.*

Example 1.6.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{56}Fe. The experimental mass of the nuclide is given in Table A4.

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

A Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of ^{1}H atoms (because its mass is the same as the mass of one electron and one proton).

B Calculate the mass defect by subtracting the experimental mass from the calculated mass.

C Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

Solution

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 ^{1}H atoms, we can calculate the sum of the masses more quickly as follows:

$$\begin{aligned}\text{calculated mass} &= 26(\text{mass } {}^{1}_{1}\text{H}) + 30(\text{mass } {}^{1}_{0}\text{n}) \\ &= 26(1.007825)\text{amu} + 30(1.008665)\text{amu} = 56.463400 \text{ amu} \\ \text{experimental mass} &= 55.934938\end{aligned}$$

B We subtract to find the mass defect:

$$\begin{aligned}\text{mass defect} &= \text{calculated mass} - \text{experimental mass} \\ &= 56.463400 \text{ amu} - 55.934938 \text{ amu} = 0.528462 \text{ amu}\end{aligned}$$

C The nuclear binding energy is thus 0.528462 amu × 931 MeV/amu = 492 MeV. The binding energy per nucleon is 492 MeV/56 nucleons = 8.79 MeV/nucleon.

? Exercise 1.6.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{238}U.

Answer

1800 MeV/^{238}U; 7.57 MeV/nucleon

Summary

Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation. Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of ^{1}H, the experimentally determined mass of an atom is always less than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the mass defect of the nucleus. The energy corresponding to the mass defect is the nuclear binding energy, the amount of energy released when a nucleus forms from its component particles. In nuclear fission, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The critical mass is the minimum mass required to support a self-sustaining nuclear chain reaction. Nuclear fusion is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

1.6: Converting Mass to Energy- Mass Defect and Nuclear Binding Energy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.5: Energy Changes in Nuclear Reactions** is licensed CC BY-NC-SA 3.0.

1.7: Nuclear Fusion - The Power of the Sun

Learning Objectives

- Describe the nuclear reactions in a nuclear fusion reaction
- Quantify the energy released or absorbed in a fusion reaction

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:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{n} \tag{1.7.1}$$

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 ${}^{4}_{2}\mathrm{He}$ 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, ${}^{2}_{1}H$ and a triton, ${}^{3}_{1}H$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{1.7.2}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^{9} kilojoules per mole of ${}^{4}_{2}\mathrm{He}$ 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.

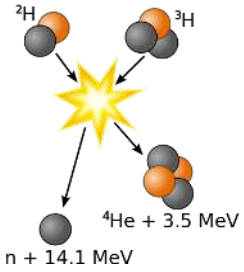


Figure 1.7.1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 1.7.2).

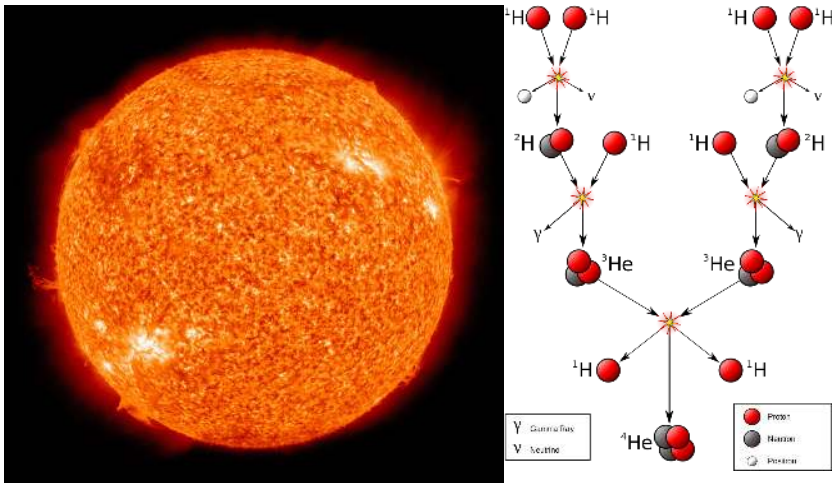


Figure 1.7.2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 1.7.1

Calculate the energy released in each of the following hypothetical processes.

a. $3\,{}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C}$
b. $6\,{}^{1}_{1}\mathrm{H} + 6\,{}^{1}_{0}\mathrm{n} \rightarrow {}^{12}_{6}\mathrm{C}$
c. $6\,{}^{2}_{1}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C}$

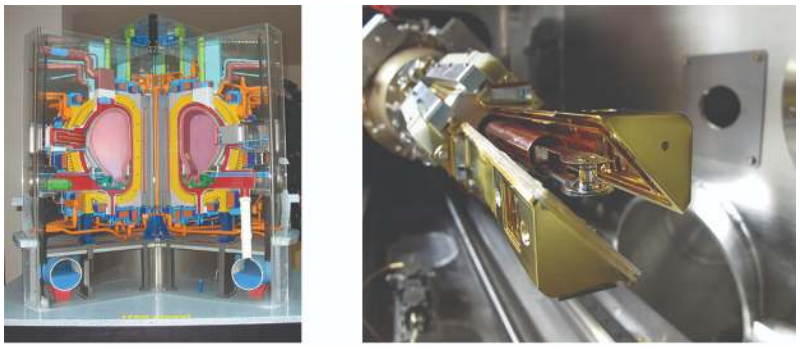
Solution

a. $Q_a = 3 \times 4.0026 - 12.000)\,amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.17 \times 10^{-12}\ J$
b. $Q_b = (6 \times (1.007825 + 1.008665) - 12.00000)\,amu \times (1.4924 \times 10^{1-0} J/amu) = 1.476 \times 10^{-11}\ J$
c. $Q_c = 6 \times 2.014102 - 12.00000\,amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.263 \times 10^{-11}\ J$

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

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.



(a) (b)

Figure 1.7.3: (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 larg\times 10^{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)

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 1.7.3). 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.Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

1.7: Nuclear Fusion - The Power of the Sun is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **25.9: Nuclear Fusion** is licensed CC BY-NC-SA 4.0.

1.8: Nuclear Transmutation and Transuranium Elements

Learning Objectives

- Describe the synthesis of transuranium nuclides

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. Science 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:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ 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.

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 1.8.1). 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 1.8.1: 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 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

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:

$$\begin{aligned} {}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} &\longrightarrow {}^{239}_{92}\mathrm{U} \\ {}^{239}_{92}\mathrm{U} &\longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \qquad \text{half-life} = 23.5 \text{ min} \\ {}^{239}_{93}\mathrm{Np} &\longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e} \qquad \text{half-life} = 2.36 \text{ days} \end{aligned}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay 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. It is possible to summarize these equations as:

$${}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu} \tag{1.8.1}$$

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 1.8.1.

Table 1.8.1: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	${}^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{240}_{95}\mathrm{Am} + {}^{0}_{-1}\mathrm{e}$
curium	Cm	96	${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
californium	Cf	98	${}^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{243}_{97}\mathrm{Bk} + 2\,{}^{1}_{0}\mathrm{n}$
einsteinium	Es	99	${}^{238}_{92}\mathrm{U} + 15\,{}^{1}_{0}\mathrm{n} \longrightarrow {}^{253}_{99}\mathrm{Es} + 7\,{}^{0}_{-1}\mathrm{e}$
mendelevium	Md	101	${}^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
nobelium	No	102	${}^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}\mathrm{n}$
rutherfordium	Rf	104	${}^{249}_{98}\mathrm{Cf} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{257}_{104}\mathrm{Rf} + 4\,{}^{1}_{0}\mathrm{n}$
seaborgium	Sg	106	${}^{206}_{82}\mathrm{Pb} + {}^{54}_{24}\mathrm{Cr} \longrightarrow {}^{257}_{106}\mathrm{Sg} + 3\,{}^{1}_{0}\mathrm{n}$ ${}^{249}_{98}\mathrm{Cf} + {}^{18}_{8}\mathrm{O} \longrightarrow {}^{263}_{106}\mathrm{Sg} + 4\,{}^{1}_{0}\mathrm{n}$
meitnerium	Mt	107	${}^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

1.8: Nuclear Transmutation and Transuranium Elements is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.9: The Effects of Radiation on Life

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{1.9.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 1.9.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1\ \text{MeV/particle} = 96\ \text{billion J/mol}.$$



Figure 1.9.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue. (CC BY-SA-NC; anonymous)

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 1.9.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

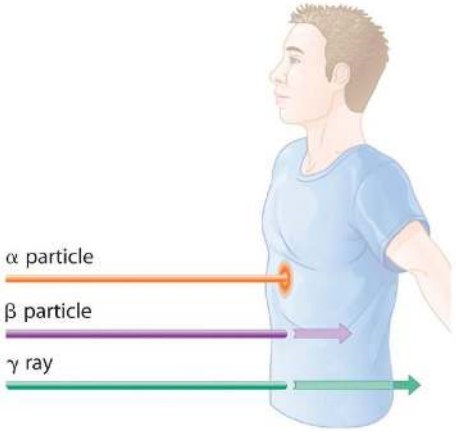


Figure 1.9.2: Depth of Penetration of Ionizing Radiation. The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed. (CC BY-SA-NC; anonymous)

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 1.9.1.

Table 1.9.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m

*Distance at which half of the radiation has been absorbed.

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \qquad 1 \text{ Gy} = 1 \text{ J/kg} \tag{1.9.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because

the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 1.9.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

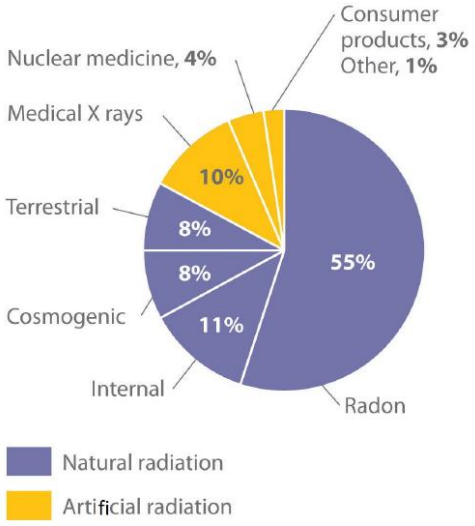


Figure 1.9.3: The Radiation Exposure of a Typical Adult in the United States. The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each. Data source: Office of Civilian Radioactive Waste Management (CC BY-SA-NC; anonymous)

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{1.9.3}$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000

^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as ^{232}Th and ^{238}U as well as radioactive daughter isotopes, such as^{226}Ra. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% ^{40}K, which decays by emitting both a β particle and a (\gamma\) ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 ^{40}K nuclei disintegrated in your body.

By far the most important source of background radiation is radon, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of^{238}U, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\alpha + {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\alpha + {}^{214}_{82}\mathrm{Pb} \tag{1.9.4}$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of ^{218}Po releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The ^{218}Po isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

✔ Example 1.9.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A. Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.
B. Determine the number of decays per year for this amount of ^{40}K.
C. Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$\text{moles } ^{40}\text{K} = 140 \text{ g K} \times \frac{0.0117 \text{ mol } ^{40}\text{K}}{100 \text{ mol K}} \times \frac{1 \text{ mol K}}{40.0 \text{ g K}} = 4.10 \times 10^{-4} \text{ mol } ^{40}\text{K}$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$\frac{\text{decays}}{\text{year}} = 4.10 \times 10^{-4} \text{ mol}^{40} \text{ K} \times \frac{1.05 \times 10^{7} \text{ decays/s}}{1.00 \text{ mol } ^{40}\text{K}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$\begin{aligned} \text{total energy per year } &= \frac{1.36 \times 10^{11} \text{ decays}}{\text{yr}} \times \frac{1.32 \text{ MeV}}{\text{decays}} \times \frac{10^{6} \text{ eV}}{\text{MeV}} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} \\ &= 2.87 \times 10^{-2} \text{ J/yr} \end{aligned}$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\begin{aligned} \text{radiation dose per year} &= \frac{2.87 \times 10^{-2} \text{ J/yr}}{70.0 \text{ kg}} \times \frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \\ &= 4.10 \times 10^{-2} \text{ rad/yr} = 41 \text{ mrad/yr} \end{aligned}$$

This corresponds to almost half of the normal background radiation most people experience.

? Exercise 1.9.1

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer

5.7×10^{3} rad/yr (which is 10 times the fatal dose)

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 1.9.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 1.9.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure 1.9.4, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

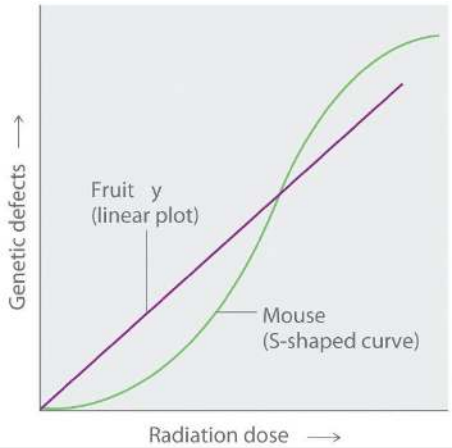


Figure 1.9.4: Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure. Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate. (CC BY-SA-NC; anonymous)

Graph of genetic defects against radiation dose. Fruit is graphed in purple and has a linear plot. Mouse is graphed in green and has a S shaped curve.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include cosmic radiation, consisting of high-energy particles and γ rays emitted by the sun and other stars; cosmogenic radiation, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and terrestrial radiation, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

1.9: The Effects of Radiation on Life is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.8: Biological Effects of Radiation** by Anonymous is licensed CC BY-NC-SA 3.0.

1.10: Radioactivity in Medicine and Other Applications

Learning Objectives

- 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.

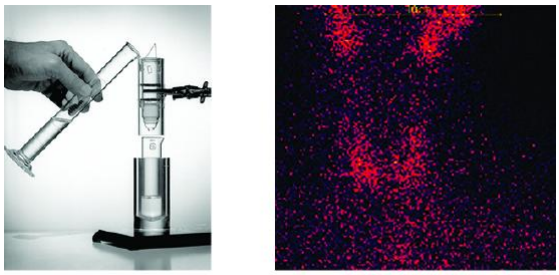
Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), 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 1.10.1) 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 1.10.1: 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)

A medical professional is assisting a topless elderly man on a treadmill with sensors and electrical wires connected to his torso.

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 1.10.2). 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.



(a) (b)

Figure 1.10.2: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The MoO_4^{2-} *is retained by the matrix in the column, whereas the* TcO_4^- *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)*

The first image shows a hand pouring a liquid from a measuring cylinder into a column held up by a clamp. Below the column is a glass tube. The second picture shows red dots on a dark background dispersed everywhere with four spots of heavily concentrated regions.

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 1.10.3). 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.

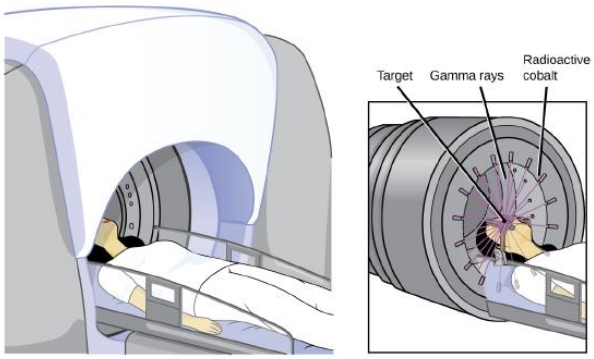


Figure 1.10.3: The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

A. A woman lies down as she goes into a dome shaped medical machine. B. A closer view of the women's head shows gamma rays from radioactive cobalt attacks the target on the woman's head.

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:

$$^{59}_{27}\mathrm{Co} + ^{1}_{0}\mathrm{n} \longrightarrow ^{60}_{27}\mathrm{Co} \longrightarrow ^{60}_{28}\mathrm{Ni} + ^{0}_{-1}\beta + 2\,^{0}_{0}\gamma$$

The overall decay scheme for this is shown graphically in Figure 1.10.4

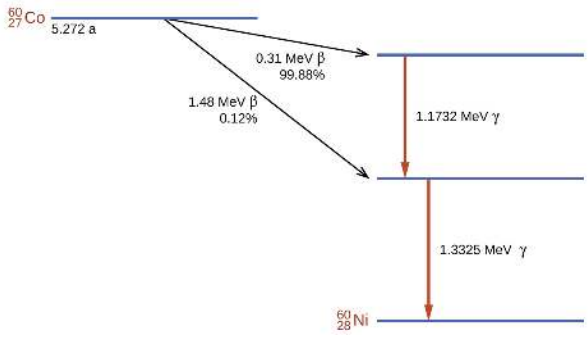


Figure 1.10.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

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:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g),$$

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 1.10.5). 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.

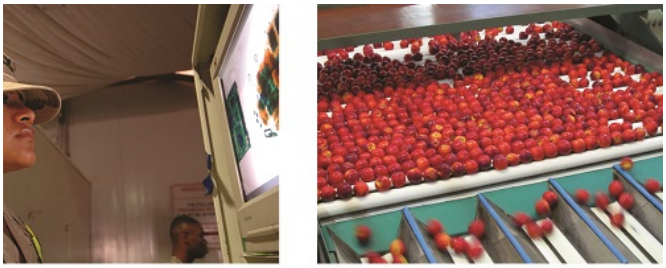


Figure 1.10.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

A. A man is observing a monitor which shows the X-ray of luggages. B. Many apples on processing belts.

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 1.10.6). 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.

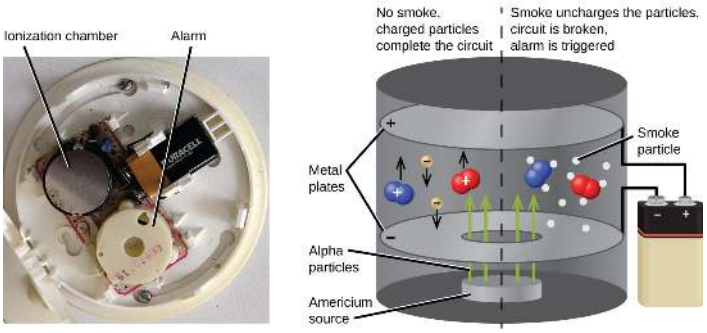


Figure 1.10.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

The inside of a smoke detector is shown with the alarm and ionization chamber labeled. In the picture beside it, a schematic shows the mechanisms of a smoke detector. The two oppositely charged metals plates in the detector are shown along with the Americium source on the bottom part emitting alpha particles. The schematic is divided into two parts, one to show the presence and the other for the absence of smoke.

Summary

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.

Glossary

chemotherapy
similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

external beam radiation therapy
radiation delivered by a machine outside the body

internal radiation therapy
(also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

radiation therapy
use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive tracer
(also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

---

1.10: Radioactivity in Medicine and Other Applications is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **21.5: Uses of Radioisotopes** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.11: 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

---

1.11: 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.

1.12: Key Equations

$E = mc^2$

decay rate = λN

rem = RBE rad
Sv = RBE Gy

1.12: 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.

1.13: 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.

1.13: 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.

1.14: Exercises

1. Write the following isotopes in hyphenated form (e.g., “carbon-14”)

(a) $^{24}_{11}\text{Na}$
(b) $^{29}_{13}\text{Al}$
(c) $^{73}_{36}\text{Kr}$
(d) $^{194}_{77}\text{Ir}$

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) $^{34}_{14}\text{X}$
(b) $^{36}_{\text{X}}\text{P}$
(c) $^{57}_{\text{X}}\text{Mn}$
(d) $^{121}_{56}\text{X}$

4. For each of the isotopes in 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}Bi
d. ^{56}Fe
e. ^{206}Pb
f. ^{211}Pb
g. ^{222}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}Ba
d. ^{58}Ni
e. ^{205}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) $^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow \ ? + {}^{1}_{0}\mathrm{n}$
(b) $^{239}_{94}\mathrm{Pu} + ? \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
(c) $^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow ? + {}^{1}_{1}\mathrm{H}$
(d) $^{235}_{92}\mathrm{U} \rightarrow ? + {}^{135}_{55}\mathrm{Cs} + 4{}^{1}_{0}\mathrm{n}$

14. Complete each of the following equations:

(a) $^{7}_{3}\mathrm{Li} + ? \rightarrow 2{}^{4}_{2}\mathrm{He}$
(b) $^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + \ ?$
(c) $^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow ? + {}^{1}_{0}\mathrm{n}$
(d) $^{250}_{96}\mathrm{Cm} \rightarrow ? + {}^{98}_{38}\mathrm{Sr} + 4{}^{1}_{0}\mathrm{n}$

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 stepwise 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 stepwise 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 1.14: 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.

CHAPTER OVERVIEW

2: Chemical Bonding and Molecular Geometry

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. All bonds can be explained by quantum theory, but, in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic orbitals molecular orbital method. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

2.1: Introduction
2.2: Ionic Bonding
2.3: Covalent Bonding
2.4: Lewis Symbols and Structures
2.5: Introduction to Formal Charges and Resonance
2.6: Molecular Structure and Polarity
2.7: Key Terms
2.8: Key Equations
2.9: Summary
2.10: Exercises

This page titled 2: Chemical Bonding and Molecular Geometry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

2.1: Introduction

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene. This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60}, and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.



Figure 2.1.1: Nicknamed “buckyballs,” buckminsterfullerene molecules (C_{60}) contain only carbon atoms (left) arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by “Petey21”/Wikimedia Commons; credit right: modification of work by Bill Morrow)

This page titled 2.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

2.2: Ionic Bonding

Learning Objectives

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

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 2.2.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure 2.2.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by “Jurii”/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3,

indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, (2 +3) + (3 –2) = 0].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure 2.2.2).

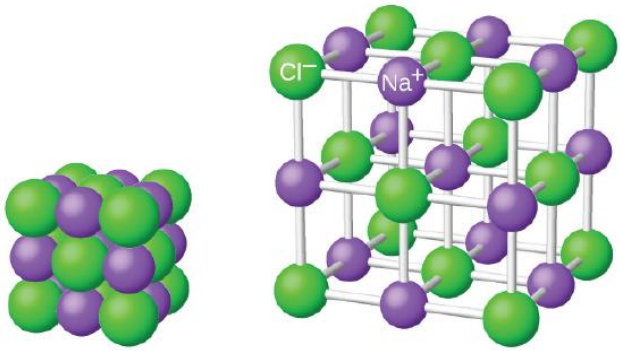


Figure 2.2.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl(s)} \longrightarrow \mathrm{Na^+(g) + Cl^-(g)} \qquad \Delta H = 769\ \mathrm{kJ}$$

Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^22s^22p^63s^23p^63d^64s^2$) forms the ion Fe^{2+} ($1s^22s^22p^63s^23p^63d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^22s^22p^63s^23p^63d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron

configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 2.2.1: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

Zn: $[Ar]3d^{10}4s^2$

Cr: $[Ar]3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

Zn^{2+}: $[Ar]3d^{10}$

Cr^{3+}: $[Ar]3d^3$

Exercise 2.2.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer

K^+: [Ar], Mg^{2+}: [Ne]

Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

Example 2.2.1: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: $[Ar]3d^{10}4s^2 4p^6$

I^-: $[Kr]4d^{10}5s^2 5p^6$

Exercise 2.2.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer

P: $[Ne]3s^2 3p^3$; P^{3-}: $[Ne]3s^2 3p^6$

This page titled 2.2: Ionic Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

2.3: Covalent Bonding

Learning Objectives

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

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 2.3.1 illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

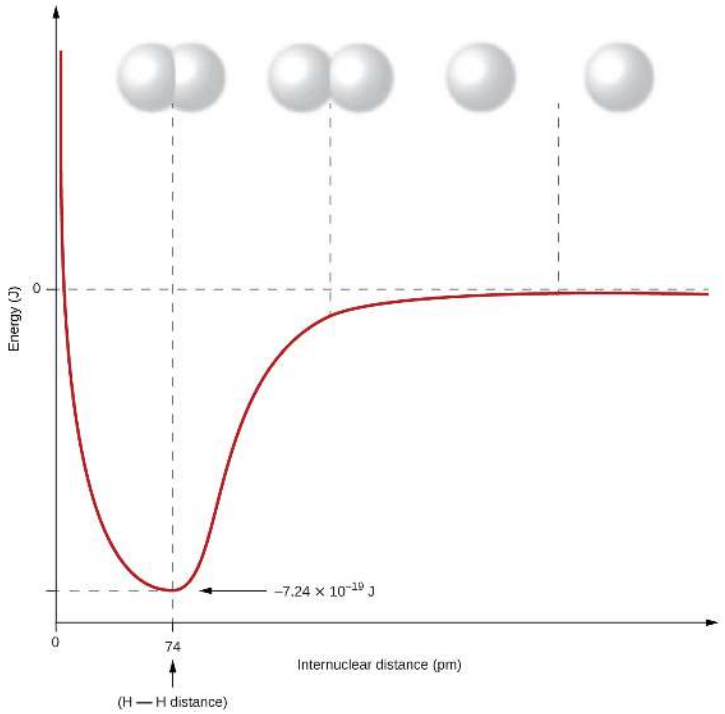


Figure 2.3.1: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2(g)} \longrightarrow 2\,\mathrm{H(g)} \quad \Delta H = 436\,\mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,\mathrm{H(g)} \longrightarrow \mathrm{H_2(g)} \quad \Delta H = -436\,\mathrm{kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl + Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 2.3.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is

much larger than it is around H. Compare this to Figure 2.3.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 2.3.2.

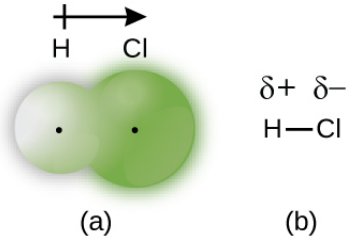


Figure 2.3.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 2.3.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 2.3.4). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

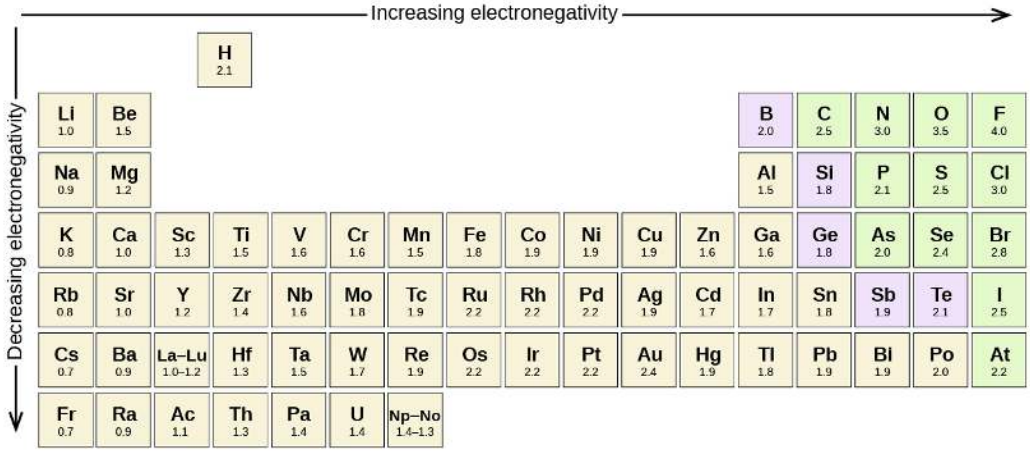


Figure 2.3.3: The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless

quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Portrait of a Chemist: Linus Pauling

Linus Pauling, shown in Figure 2.3.4, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

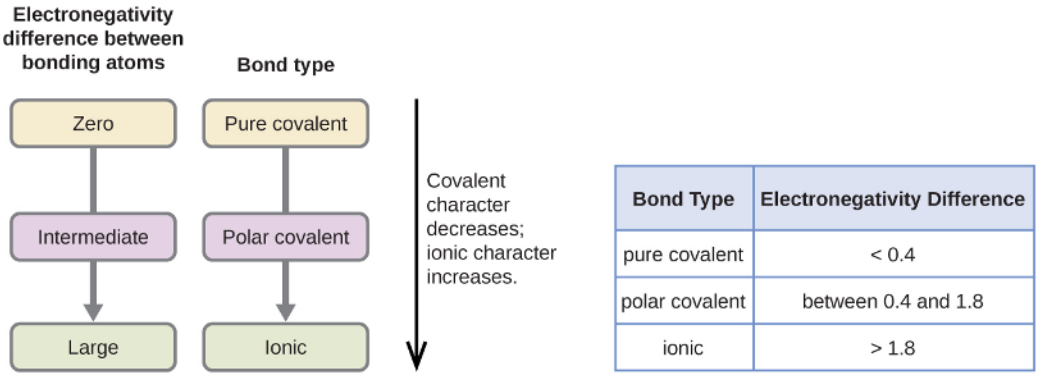


Figure 2.3.4: Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 2.3.5 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 2.3.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 2.3.5. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, and are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and as well as covalent between the nitrogen and oxygen atoms in

Example 2.3.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 2.3.3, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 2.3.1 shows these bonds in order of increasing polarity.

Table 2.3.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	
S–H	0.4	
C–N	0.5	
N–H	0.9	
C–O	1.0	
O–H	1.4	

Exercise 2.3.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 2.3.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	
Si–C	0.7	
Si–O	1.7	

This page titled 2.3: Covalent Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

2.4: Lewis Symbols and Structures

Learning Objectives

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

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure 2.4.1: shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na·
magnesium	$[Ne]3s^2$	·Mg·
aluminum	$[Ne]3s^23p^1$	·Al·
silicon	$[Ne]3s^23p^2$	·Si·
phosphorus	$[Ne]3s^23p^3$	·P·
sulfur	$[Ne]3s^23p^4$	:S·
chlorine	$[Ne]3s^23p^5$	:Cl·
argon	$[Ne]3s^23p^6$	:Ar:

Figure 2.4.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



Figure 2.4.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

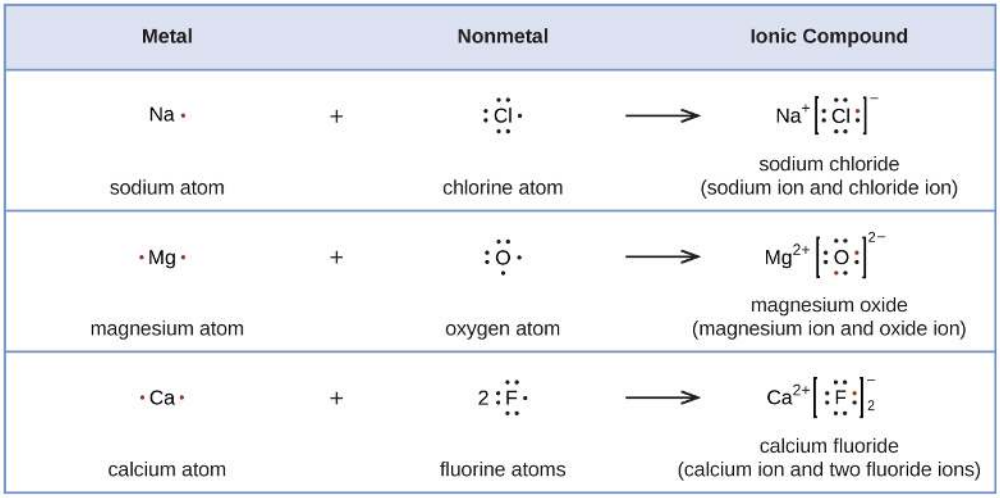
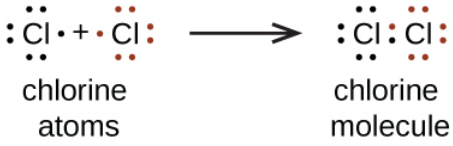


Figure 2.4.2: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

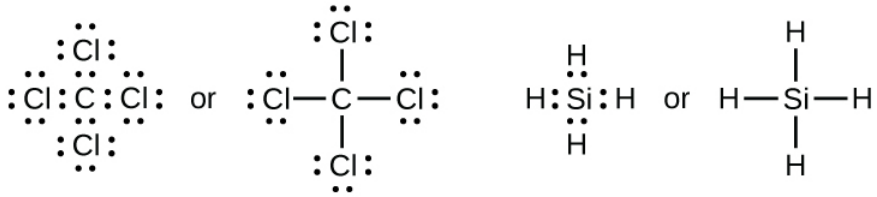


A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

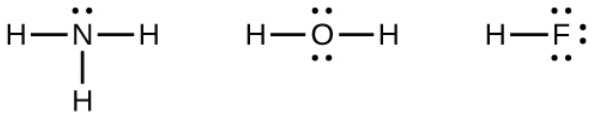
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:



carbon tetrachloride silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

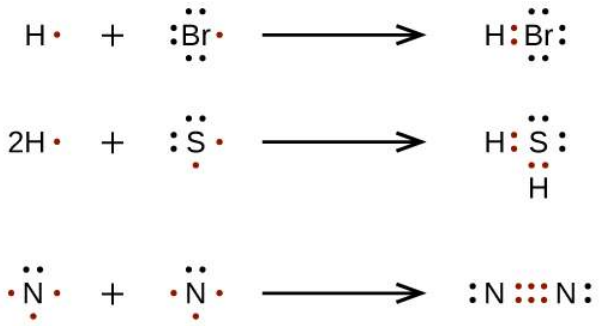
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here.

Writing Lewis Structures

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{array}{rr} & \mathrm{SiH_4} \\ \mathrm{Si:}\ 4\ \text{valence electrons/atom} \times\ 1\ \text{atom} & = 4 \\ +\quad \mathrm{H:}\ 1\ \text{valence electron/atom} \times\ 4\ \text{atoms} & = 4 \\ \hline \text{total valence electrons} & = 8 \end{array}$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{array}{rr} & \mathrm{CHO_2^-} \\ \mathrm{C:}\ 4\ \text{valence electrons/atom} \times\ 1\ \text{atom} & = 4 \\ \mathrm{H:}\ 1\ \text{valence electron/atom} \times\ 1\ \text{atoms} & = 1 \\ \mathrm{O:}\ 6\ \text{valence electron/atom} \times\ 2\ \text{atoms} & = 12 \\ +\quad 1\ \text{electron} & = 1 \\ \hline \text{total valence electrons} & = 18 \end{array}$$

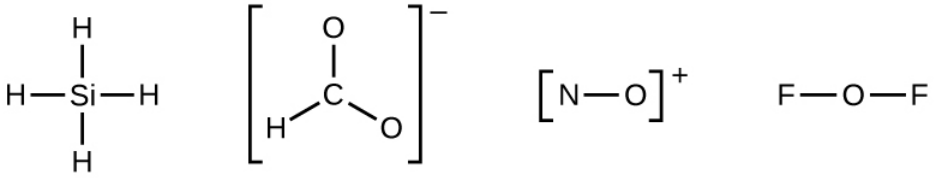
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{array}{rr} & \mathrm{NO^+} \\ \mathrm{N:}\ 5\ \text{valence electrons/atom} \times\ 1\ \text{atom} & = 5 \\ \mathrm{O:}\ 6\ \text{valence electron/atom} \times\ 1\ \text{atoms} & = 6 \\ +\quad \text{e: -1 electron (positive charge)} \times\ 1\ \text{electron} & = -1 \\ \hline \text{total valence electrons} & = 10 \end{array}$$

   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

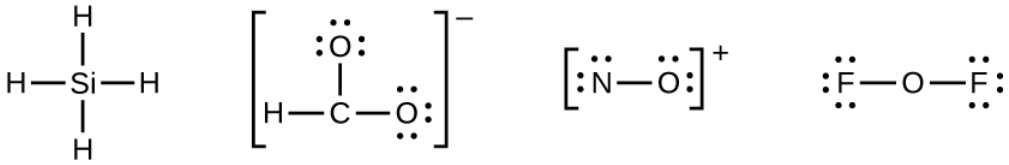
$$\begin{array}{rr} & \mathrm{OF_2} \\ \mathrm{O:\ 6\ valence\ electrons/atom} \times\ 1\ \mathrm{atom} & = 6 \\ +\quad \mathrm{F:\ 7\ valence\ electron/atom} \times\ 2\ \mathrm{atoms} & = 14 \\ \hline \mathrm{total\ valence\ electrons} & = 20 \end{array}$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)

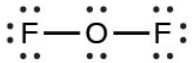


When several arrangements of atoms are possible, as for $\mathrm{CHO_2^-}$, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In $\mathrm{CHO_2^-}$, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $\mathrm{POCl_3}$, S in $\mathrm{SO_2}$, and Cl in $\mathrm{ClO_4^-}$. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

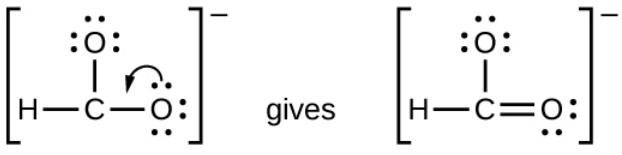
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on $\mathrm{SiH_4}$, so it is unchanged:



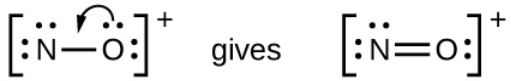
4. Place all remaining electrons on the central atom.
   - For $\mathrm{SiH_4}$, $\mathrm{CHO_2^-}$, and $\mathrm{NO^+}$, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For $\mathrm{OF_2}$, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



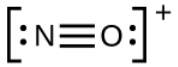
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - $\mathrm{SiH_4}$: Si already has an octet, so nothing needs to be done.
   - $\mathrm{CHO2^-}$: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



   - $\mathrm{NO^+}$: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 2.4.1: Writing Lewis Structures

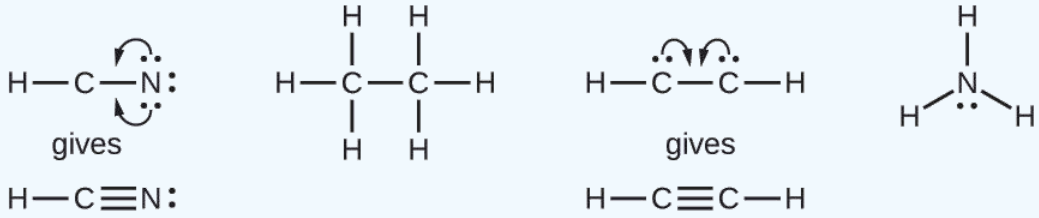
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

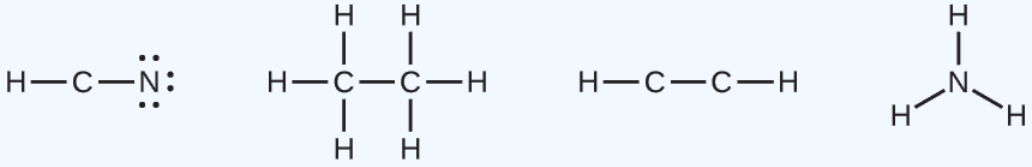
Step 1. *Calculate the number of valence electrons.*

HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
NH_3: (5 × 1) + (3 × 1) = 8

Step 2 *Draw a skeleton and connect the atoms with single bonds.* Remember that H is never a central atom:

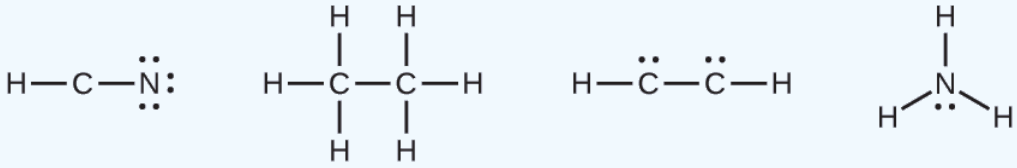


Step 3. *Where needed, distribute electrons to the terminal atoms:*



HCN: six electrons placed on N
H_3CCH_3: no electrons remain
HCCH: no terminal atoms capable of accepting electrons
NH_3: no terminal atoms capable of accepting electrons

Step 4. *Where needed, place remaining electrons on the central atom:*

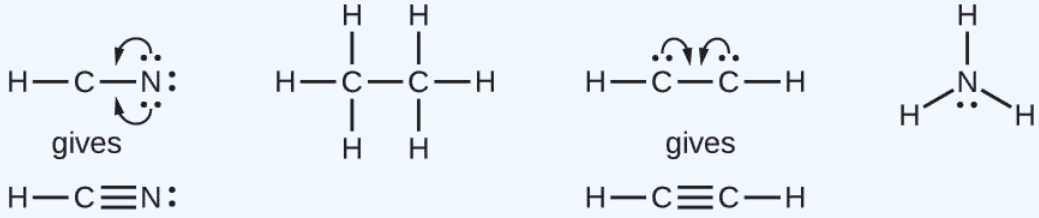


https://chem.libretexts.org/@go/page/456031

HCN: no electrons remain
H_3CCH_3: no electrons remain
HCCH: four electrons placed on carbon
NH_3: two electrons placed on nitrogen

Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

HCN: form two more C–N bonds
H_3CCH_3: all atoms have the correct number of electrons
HCCH: form a triple bond between the two carbon atoms
NH_3: all atoms have the correct number of electrons



Exercise 2.4.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



How Sciences Interconnect: Fullerene Chemistry

Carbon, in various forms and compounds, has been known since prehistoric times, . Soot has been used as a pigment (often called carbon black) for thousands of years. Charcoal, high in carbon content, has likewise been critical to human development. Carbon is the key additive to iron in the steelmaking process, and diamonds have a unique place in both culture and industry. With all this usage came significant study, particularly with the emergence of organic chemistry. And even with all the known forms and functions of the element, scientists began to uncover the potential for even more varied and extensive carbon structures.

As early as the 1960s, chemists began to observe complex carbon structures, but they had little evidence to support their concepts, or their work did not make it into the mainstream. Eiji Osawa predicted a spherical form based on observations of a similar structure, but his work was not widely known outside Japan. In a similar manner, the most comprehensive advance was likely computational chemist Elena Galpern's, who in 1973 predicted a highly stable, 60-carbon molecule; her work was also isolated to her native Russia. Still later, Harold Kroto, working with Canadian radio astronomers, sought to uncover the nature of long carbon chains that had been discovered in interstellar space.

Kroto sought to use a machine developed by Richard Smalley's team at Rice University to learn more about these structures. Together with Robert Curl, who had introduced them, and three graduate students—James Heath, Sean O'Brien, and Yuan Liu —they performed an intensive series of experiments that led to a major discovery.

In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 2.4.3), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown

potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

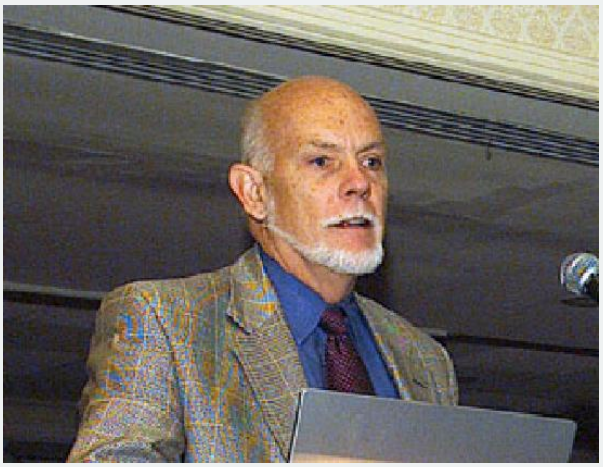


Figure 2.4.3: Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

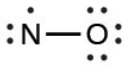
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

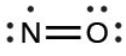
We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:
   N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

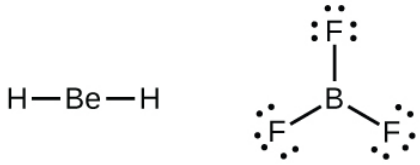


4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

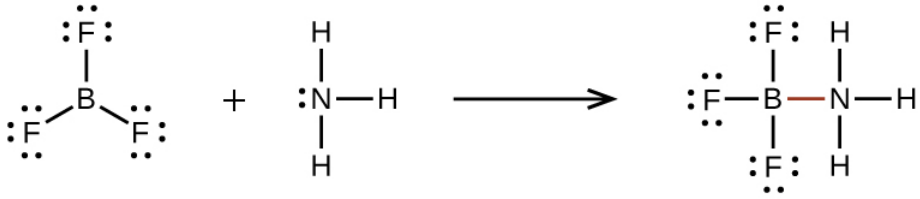


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figure 2.4.4: shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

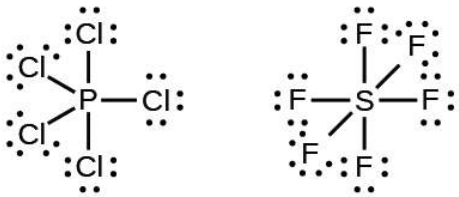
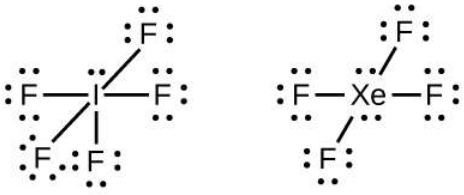


Figure 2.4.4: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 2.4.2: Writing Lewis Structures - Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

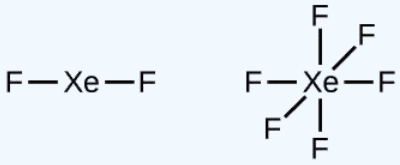
Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

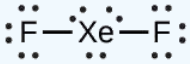
XeF_2: 8 + (2 × 7) = 22
XeF_6: 8 + (6 × 7) = 50

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

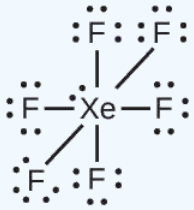


Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



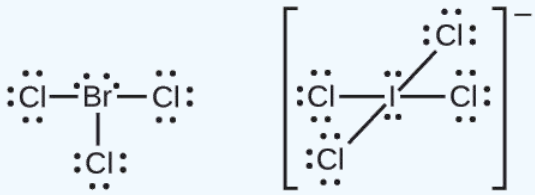
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 2.4.2: Interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Answer



This page titled 2.4: Lewis Symbols and Structures is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **7.3: Lewis Symbols and Structures** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.5: Introduction to Formal Charges and Resonance

Learning Objectives

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

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge } = \#\text{ valence shell electrons (free atom) } - \#\text{ lone pair electrons } - \frac{1}{2}\#\text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

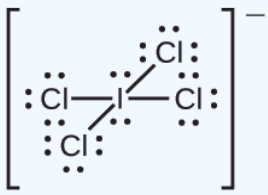
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 2.5.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion

Solution

Step 1. *We divide the bonding electron pairs equally for all I–Cl bonds:*



Step 2. *We assign lone pairs of electrons to their atoms*. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom:*

I: 7 – 8 = –1
Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

? Exercise 2.5.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

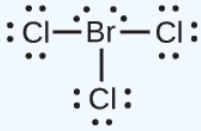
C −1, O +1

✓ Example 2.5.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Step 1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*



Step 2. *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons and the Br atom has seven electrons.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom.* This gives the formal charge:

Br: 7 – 7 = 0
Cl: 7 – 7 = 0

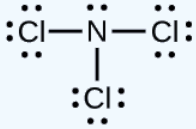
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

? Exercise 2.5.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0

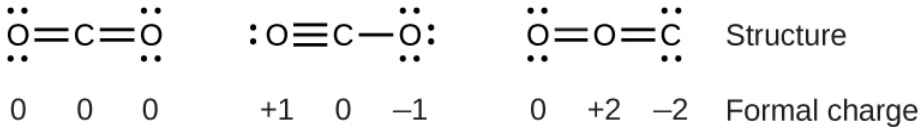


Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

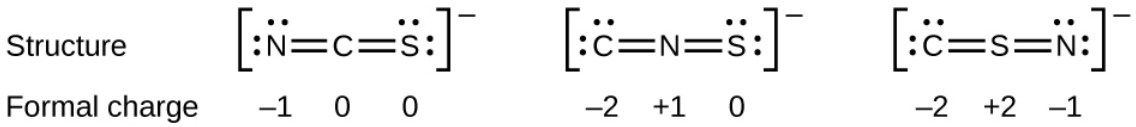
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

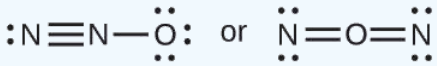
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: NCS^-, CNS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

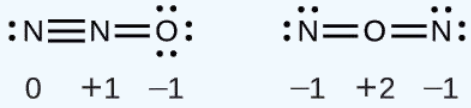
Example 2.5.3: Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the more likely structure for nitrous oxide?

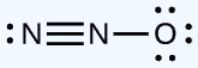


Solution

Determining formal charge yields the following:



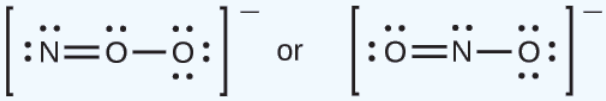
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), there is no formal charge with a magnitude greater than one (Guideline 2), the negative formal charge is on the more electronegative element (Guideline 4), and the less electronegative atom is in the center position.

Exercise 2.5.3

Which is the most likely molecular structure for the nitrite ion?



Answer

ONO^-

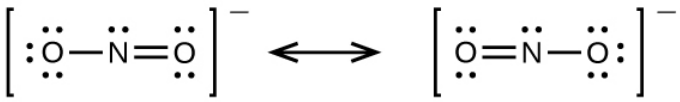
Resonance

Notice that the more likely structure for the nitrite anion in Example 2.5.3 may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:



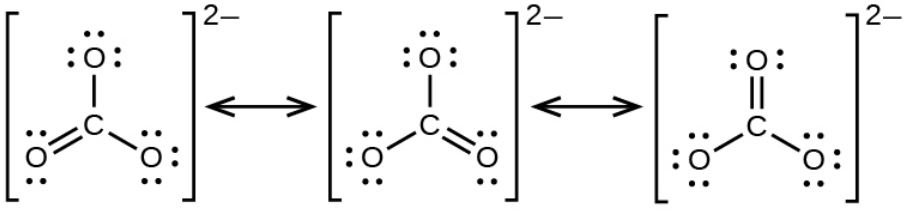
If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Link to Learning

Use this online quiz to practice your skills in drawing resonance structures and estimating formal charges.

This page titled 2.5: Introduction to Formal Charges and Resonance is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **7.4: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.6: Molecular Structure and Polarity

Learning Objectives

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

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 2.6.1). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

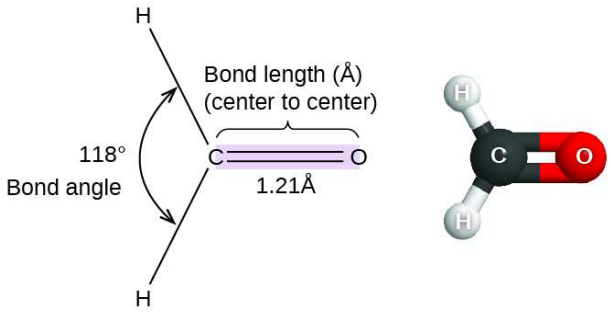


Figure 2.6.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 2.6.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 2.6.2).

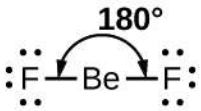


Figure 2.6.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 2.6.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

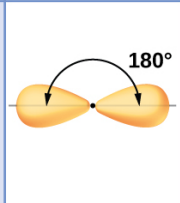
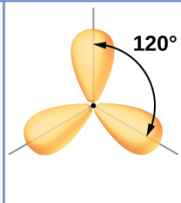
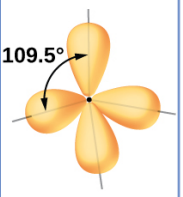
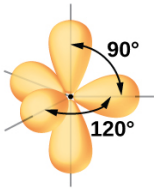
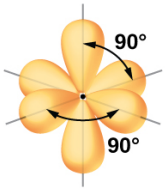
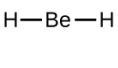
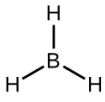
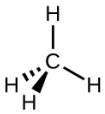
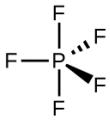
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 2.6.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 2.6.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

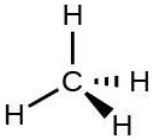


Figure 2.6.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 2.6.4). On the other hand,

the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 2.6.5).

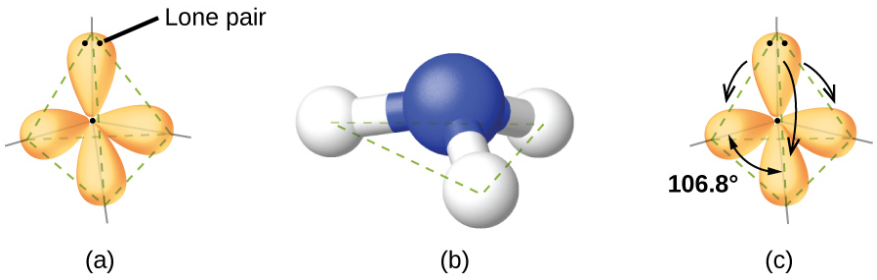


Figure 2.6.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in Figure 2.6.5, small distortions from the ideal angles in Figure 2.6.3 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

$$\text{lone pair-lone pair} > \text{lone pair-bonding pair} > \text{bonding pair-bonding pair}$$

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

$$\text{lone pair} > \text{triple bond} > \text{double bond} > \text{single bond}$$

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure 2.6.1). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 2.6.5) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 2.6.3) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 2.6.5). Figure 2.6.6 illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

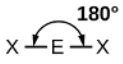
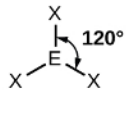
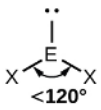
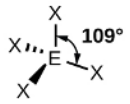
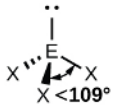
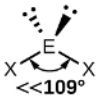
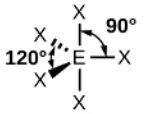
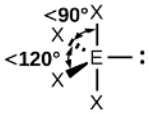
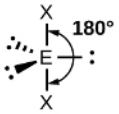
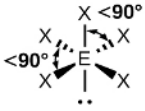
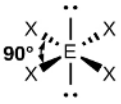
Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 2.6.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure 2.6.6) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 2.6.7 an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). As shown in Figure 2.6.6, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 2.6.7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

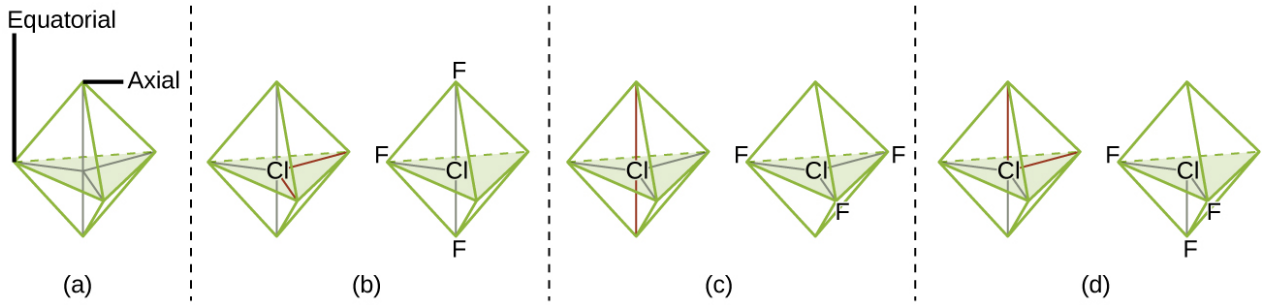


Figure 2.6.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 2.6.6).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 2.6.6, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 2.6.6). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

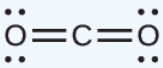
Example 2.6.1: Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

Solution

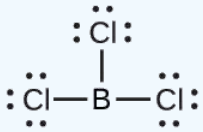
(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:

https://chem.libretexts.org/@go/page/456033



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure (Figure 2.6.8).

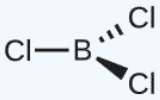


Figure 2.6.8:

The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

? Exercise 2.6.1

Carbonate, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

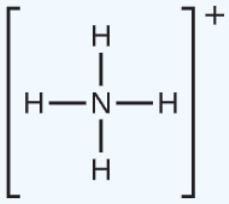
The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

✓ Example 2.6.2: Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the cation.

Solution

We write the Lewis structure of as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 2.6.6). Therefore, the electron pair geometry of Figure 2.6.9.

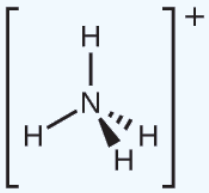


Figure 2.6.9: The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Exercise 2.6.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

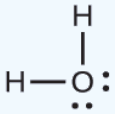
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 2.6.3: Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (Figure 2.6.10), as indicated in Figure 2.6.6. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

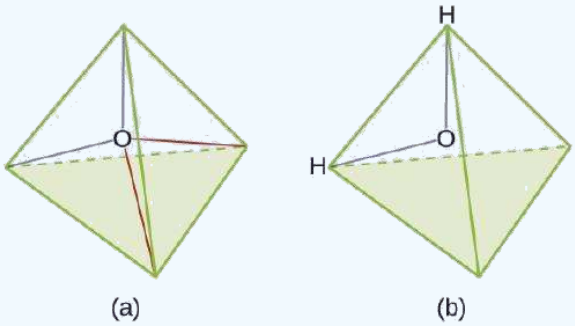


Figure 2.6.10: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 2.6.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

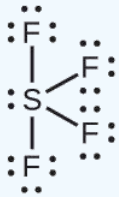
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example 2.6.4: Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure 2.6.11) is that of a seesaw (Figure 2.6.6).

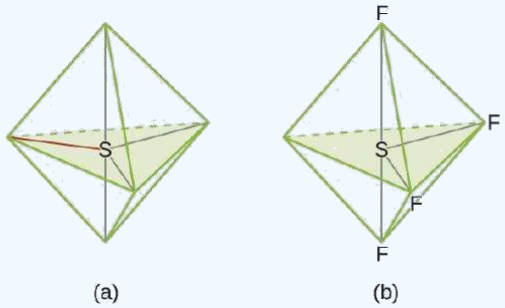


Figure 2.6.11: (a) SF4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 2.6.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Answer

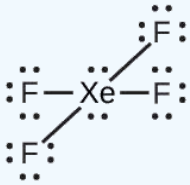
The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Example 2.6.5: Predicting Electron-pair Geometry and Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (Figure 2.6.6), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 2.6.12). The five atoms are all in the same plane and have a square planar molecular structure.

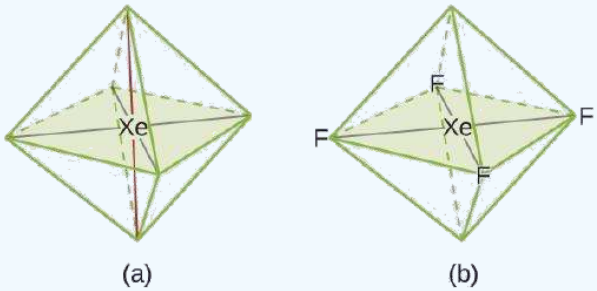


Figure 2.6.12: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Exercise 2.6.5

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Answer

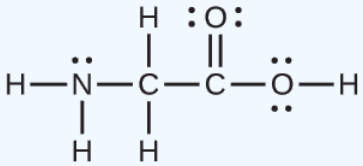
electron pair geometry: trigonal bipyramidal; molecular structure: linear

Molecular Structure for Multicenter Molecules

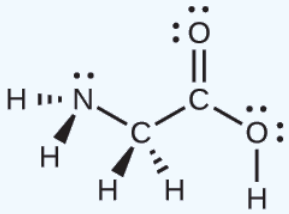
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

Example 2.6.6: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

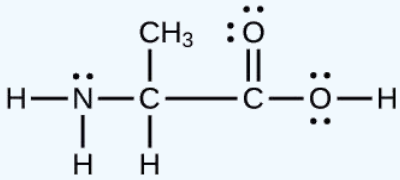
- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

Exercise 2.6.6

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

Link to Learning

The molecular shape simulator lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example 2.6.7: Molecular Simulation

Using molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$H{-}C{\equiv}N$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Exercise 2.6.7

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 2.6.13). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

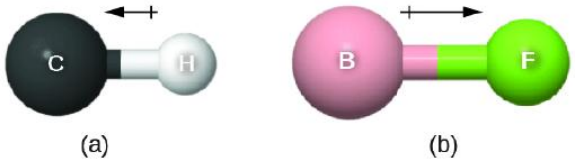


Figure 2.6.13: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 2.6.14). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 2.6.14), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

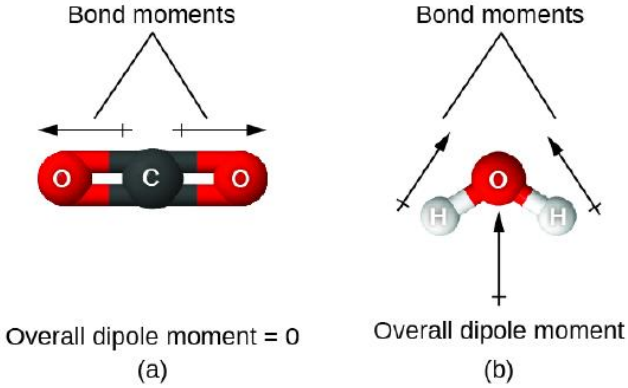
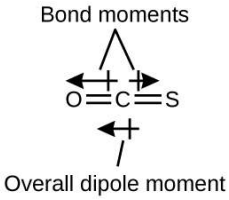


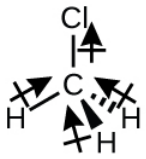
Figure 2.6.14: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

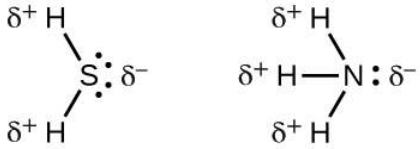


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is H < C < Cl, and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).



For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).



To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 2.6.15). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

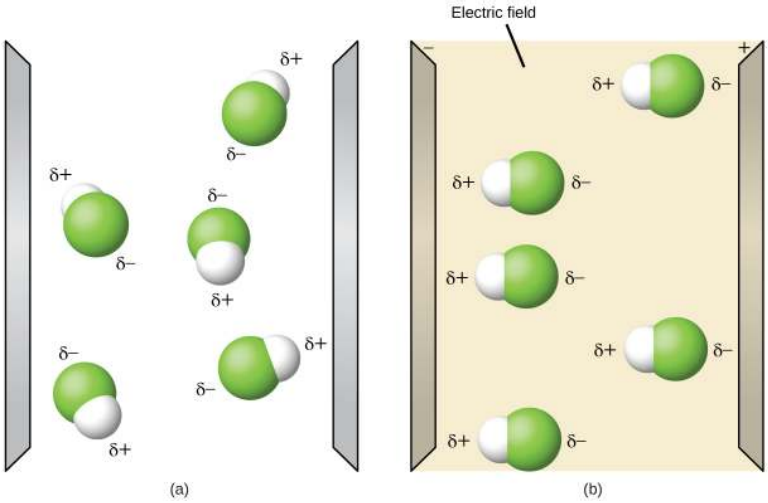


Figure 2.6.15: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Link to Learning

The molecule polarity simulation provides many ways to explore dipole moments of bonds and molecules.

Example 2.6.8: Polarity Simulations

Open the molecule polarity simulation and select the "Three Atoms" tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 2.6.15

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 2.6.8

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

This page titled 2.6: Molecular Structure and Polarity is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **7.6: Molecular Structure and Polarity** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.7: Key Terms

axial position

location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

binary acid

compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound

compound containing two different elements.

bond angle

angle between any two covalent bonds that share a common atom

bond dipole moment

separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

bond distance

(also, bond length) distance between the nuclei of two bonded atoms

bond length

distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond

bond formed when electrons are shared between atoms

dipole moment

property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

double bond

covalent bond in which two pairs of electrons are shared between two atoms

electron-pair geometry

arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

electronegativity

tendency of an atom to attract electrons in a bond to itself

equatorial position

one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

free radical

molecule that contains an odd number of electrons

hypervalent molecule

molecule containing at least one main group element that has more than eight electrons in its valence shell

inert pair effect
tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

ionic bond
strong electrostatic force of attraction between cations and anions in an ionic compound

Lewis structure
diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol
symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

linear
shape in which two outside groups are placed on opposite sides of a central atom

lone pair
two (a pair of) valence electrons that are not used to form a covalent bond

molecular structure
arrangement of atoms in a molecule or ion

molecular structure
structure that includes only the placement of the atoms in the molecule

nomenclature
system of rules for naming objects of interest

octahedral
shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

octet rule
guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

polar covalent bond
covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

polar molecule
(also, dipole) molecule with an overall dipole moment

pure covalent bond
(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

resonance
situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms
two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid
average of the resonance forms shown by the individual Lewis structures

single bond
bond in which a single pair of electrons is shared between two atoms

tetrahedral
shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal
shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar
shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

triple bond
bond in which three pairs of electrons are shared between two atoms

valence shell electron-pair repulsion theory (VSEPR)
theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector
quantity having magnitude and direction

This page titled 2.7: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

2.8: Key Equations

$$\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ lone pair electrons} - \tfrac{1}{2}\ \#\text{ bonding}$$

This page titled 2.8: Key Equations is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

2.9: Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*–ate* to *–ic* and *–ite* to *–ous*), and adding "acid;" H_2CO_3 is carbonic acid.

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

This page titled 2.9: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

2.10: Exercises

1.

Does a cation gain protons to form a positive charge or does it lose electrons?

2.

Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and $SO_4{}^{2-}$ ions. Explain why a sample of iron(III) sulfate is uncharged.

3.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

4.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

5.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) P

(b) Mg

(c) Al

(d) O

(e) Cl

(f) Cs

6.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) I

(b) Sr

(c) K

(d) N

(e) S

(f) In

7.

Write the electron configuration for each of the following ions:

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) Cd^{2+}

(e) O^{2-}

(f) Ga^{3+}

(g) Li^{+}

(h) N^{3-}

(i) Sn^{2+}

(j) Co^{2+}

(k) Fe^{2+}

(l) As^{3+}

8.

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

9.

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

(a) Al

(b) Br

(c) Sr

(d) Li

(e) As

(f) S

10.

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

11.

Why is it incorrect to speak of a molecule of solid NaCl?

12.

What information can you use to predict whether a bond between two atoms is covalent or ionic?

13.

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

(a) Cl_2CO

(b) MnO

(c) NCl_3

(d) $CoBr_2$

(e) K_2S

(f) CO

(g) CaF_2

(h) HI

(i) CaO

(j) IBr

(k) CO_2

14.

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

15.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) Br or Cl

(b) N or O

(c) S or O

(d) P or S

(e) Si or N

(f) Ba or P

(g) N or K

16.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) N or P

(b) N or Ge

(c) S or F

(d) Cl or S

(e) H or C

(f) Se or P

(g) C or Si

17.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, H, N, O

(b) Br, Cl, F, H, I

(c) F, H, O, P, S

(d) Al, H, Na, O, P

(e) Ba, H, N, O, As

18.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) As, H, N, P, Sb

(b) Cl, H, P, S, Si

(c) Br, Cl, Ge, H, Sr

(d) Ca, H, K, N, Si

(e) Cl, Cs, Ge, H, Sr

19.

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

20.

Which is the most polar bond?

(a) C–C

(b) C–H

(c) N–H

(d) O–H

(e) Se–H

21.

Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCl

(b) NO or CO

(c) SH or OH

(d) PCl or SCl

(e) CH or NH

(f) SO or PO

(g) CN or NN

22.

Which of the following molecules or ions contain polar bonds?

(a) O_3

(b) S_8

(c) O_2^{2-}

(d) NO_3^-

(e) CO_2

(f) H_2S

(g) BH_4^-

23.

Name the following compounds:

(a) CsCl

(b) BaO

(c) K_2S

(d) $BeCl_2$

(e) HBr

(f) AlF_3

24.

Name the following compounds:

(a) NaF

(b) Rb_2O

(c) BCl_3

(d) H_2Se

(e) P_4O_6

(f) ICl_3

25.

Write the formulas of the following compounds:

(a) rubidium bromide

(b) magnesium selenide

(c) sodium oxide

(d) calcium chloride

(e) hydrogen fluoride

(f) gallium phosphide

(g) aluminum bromide

(h) ammonium sulfate

26.

Write the formulas of the following compounds:

(a) lithium carbonate

(b) sodium perchlorate

(c) barium hydroxide

(d) ammonium carbonate

(e) sulfuric acid

(f) calcium acetate

(g) magnesium phosphate

(h) sodium sulfite

27.

Write the formulas of the following compounds:

(a) chlorine dioxide

(b) dinitrogen tetraoxide

(c) potassium phosphide

(d) silver(I) sulfide

(e) aluminum fluoride trihydrate

(f) silicon dioxide

28.

Write the formulas of the following compounds:

(a) barium chloride

(b) magnesium nitride

(c) sulfur dioxide

(d) nitrogen trichloride

(e) dinitrogen trioxide

(f) tin(IV) chloride

29.

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) Cr_2O_3

(b) $FeCl_2$

(c) CrO_3

(d) $TiCl_4$

(e) $CoCl_2 \cdot 6H_2O$

(f) MoS_2

30.

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) $NiCO_3$

(b) MoO_3

(c) $Co(NO_3)_2$

(d) V_2O_5

(e) MnO_2

(f) Fe_2O_3

31.

The following ionic compounds are found in common household products. Write the formulas for each compound:

(a) potassium phosphate

(b) copper(II) sulfate

(c) calcium chloride

(d) titanium(IV) oxide

(e) ammonium nitrate

(f) sodium bisulfate (the common name for sodium hydrogen sulfate)

32.

The following ionic compounds are found in common household products. Name each of the compounds:

(a) $Ca(H_2PO_4)_2$

(b) $FeSO_4$

(c) $CaCO_3$

(d) MgO

(e) $NaNO_2$

(f) KI

33.

What are the IUPAC names of the following compounds?

(a) manganese dioxide

(b) mercurous chloride (Hg_2Cl_2)

(c) ferric nitrate [$Fe(NO_3)_3$]

(d) titanium tetrachloride

(e) cupric bromide ($CuBr_2$)

34.

Write the Lewis symbols for each of the following ions:

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) O^{2-}

(e) Ga^{3+}

(f) Li^+

(g) N^{3-}

35.

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

36.

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b) Al_2O_3

(c) $GaCl_3$

(d) K_2O

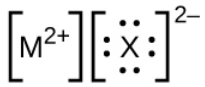
(e) Li_3N

(f) KF

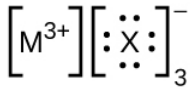
37.

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

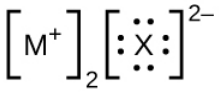
(a)



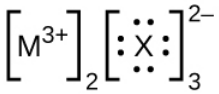
(b)



(c)



(d)



38.

Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

39.

Write Lewis structures for the following:

(a) H_2

(b) HBr

(c) PCl_3

(d) SF_2

(e) H_2CCH_2

(f) HNNH

(g) H_2CNH

(h) NO^-

(i) N_2

(j) CO

(k) CN^-

40.

Write Lewis structures for the following:

(a) O_2

(b) H_2CO

(c) AsF_3

(d) ClNO

(e) $SiCl_4$

(f) H_3O^+

(g) $NH_4{}^+$

(h) $BF_4{}^-$

(i) HCCH

(j) ClCN

(k) $C_2{}^{2+}$

41.

Write Lewis structures for the following:

(a) ClF_3

(b) PCl_5

(c) BF_3

(d) $PF_6{}^-$

42.

Write Lewis structures for the following:

(a) SeF_6

(b) XeF_4

(c) $SeCl_3{}^+$

(d) Cl_2BBCl_2 (contains a B–B bond)

43.

Write Lewis structures for:

(a) PO_4^{3-}

(b) ICl_4^-

(c) SO_3^{2-}

(d) HONO

44.

Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

45.

Write Lewis structures for the following molecules or ions:

(a) SbH_3

(b) XeF_2

(c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

46.

Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

47.

Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

48.

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

49.

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

(a) $1s^2 2s^2 2p^5$

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

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

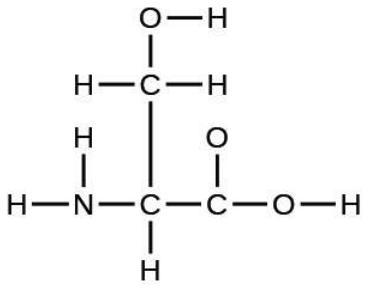
(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

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

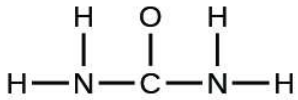
50.

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

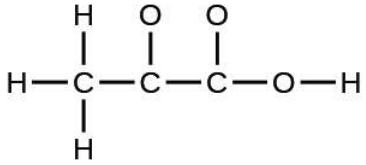
(a) the amino acid serine:



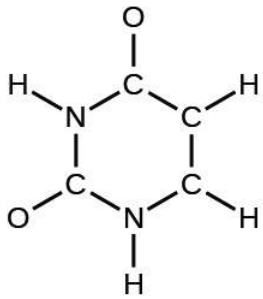
(b) urea:



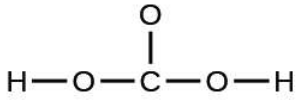
(c) pyruvic acid:



(d) uracil:



(e) carbonic acid:



51.

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

52.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

53.

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

54.

How are single, double, and triple bonds similar? How do they differ?

55.

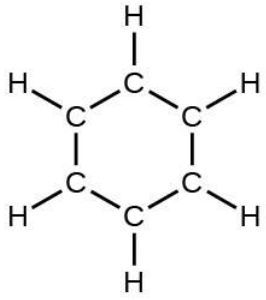
Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) selenium dioxide, OSeO

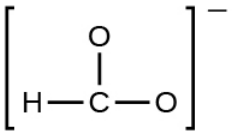
(b) nitrate ion, NO_3^-

(c) nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)

(d) benzene, C_6H_6:



(e) the formate ion:



56.

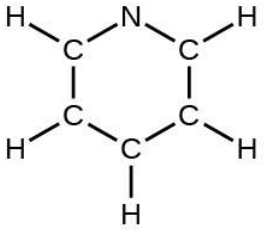
Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) sulfur dioxide, SO_2

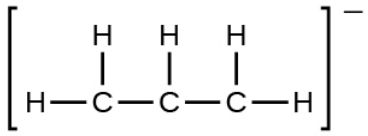
(b) carbonate ion, CO_3^{2-}

(c) hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

(d) pyridine:



(e) the allyl ion:



57.

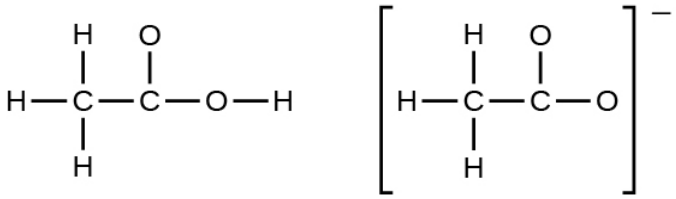
Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

58.

Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^-.

59.

In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



60.

Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

(a) CO_2

(b) CO

61.

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

62.

Determine the formal charge of each element in the following:

(a) HCl

(b) CF_4

(c) PCl_3

(d) PF_5

63.

Determine the formal charge of each element in the following:

(a) H_3O^+

(b) SO_4^{2-}

(c) NH_3

(d) O_2^{2-}

(e) H_2O_2

64.

Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

65.

Calculate the formal charge of each element in the following compounds and ions:

(a) F_2CO

(b) NO^-

(c) BF_4^-

(d) $SnCl_3^-$

(e) H_2CCH_2

(f) ClF_3

(g) SeF_6

(h) PO_4^{3-}

66.

Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

(a) O_3

(b) SO_2

(c) NO_2^-

(d) NO_3^-

67.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

68.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

69.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

70.

Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

71.

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

(a) IF

(b) IF_3

(c) IF_5

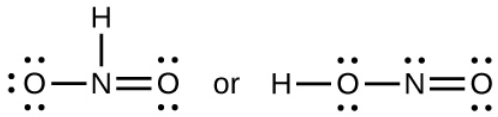
(d) IF_7

72.

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

73.

Which of the following structures would we expect for nitrous acid? Determine the formal charges:



74.

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur.

75.

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

76.

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

77.

Explain the difference between electron-pair geometry and molecular structure.

78.

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?

79.

Explain how a molecule that contains polar bonds can be nonpolar.

80.

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

81.

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) SF_6

(b) PCl_5

(c) BeH_2

(d) CH_3^+

82.

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) IF_6^+

(b) CF_4

(c) BF_3

(d) SiF_5^-

(e) $BeCl_2$

83.

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^{2-}$

(d) PCl_3

(e) SeF_4

(f) PH_2^-

84.

Predict the electron pair geometry and the molecular structure of each of the following ions:

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^+$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

85.

Identify the electron pair geometry and the molecular structure of each of the following molecules:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

86.

Predict the electron pair geometry and the molecular structure of each of the following:

(a) IOF_5 (I is the central atom)

(b) $POCl_3$ (P is the central atom)

(c) Cl_2SeO (Se is the central atom)

(d) $ClSO^+$ (S is the central atom)

(e) F_2SO (S is the central atom)

(f) NO_2^-

(g) SiO_4^{4-}

87.

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^{2-}$

(d) PCl_3

(e) SeF_4

(f) PH_2^-

(g) XeF_2

88.

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^-$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

89.

Which of the following molecules have dipole moments?

(a) CS_2

(b) SeS_2

(c) CCl_2F_2

(d) PCl_3 (P is the central atom)

(e) ClNO (N is the central atom)

90.

Identify the molecules with a dipole moment:

(a) SF_4

(b) CF_4

(c) Cl_2CCBr_2

(d) CH_3Cl

(e) H_2CO

91.

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

92.

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

93.

Is the Cl_2BBCl_2 molecule polar or nonpolar?

94.

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

95.

Describe the molecular structure around the indicated atom or atoms:

(a) the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]

(b) the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]

(c) the oxygen atom in hydrogen peroxide, HOOH

(d) the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]

(e) the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]

(f) the central oxygen atom in the ozone molecule, O_3

(g) each of the carbon atoms in propyne, CH_3CCH

(h) the carbon atom in Freon, CCl_2F_2

(i) each of the carbon atoms in allene, H_2CCCH_2

96.

Draw the Lewis structures and predict the shape of each compound or ion:

(a) CO_2

(b) NO_2^-

(c) SO_3

(d) SO_3^{2-}

97.

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

98.

A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

99.

Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

(a) CS_3^{2-}

(b) CS_2

(c) CS

(d) predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

100.

What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

101.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

102.

Use the simulation to perform the following exercises for a two-atom molecule:

(a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.

(b) With a partial positive charge on A, turn on the electric field and describe what happens.

(c) With a small partial negative charge on A, turn on the electric field and describe what happens.

(d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

103.

Use the simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

(a) Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.

(b) Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

104.

Use the Molecule Shape simulator to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

105.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the “real” and “model” modes. Explain the difference observed.

106.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O. What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

This page titled 2.10: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

3: Advanced Theories of Covalent Bonding

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields.

3.1: Introduction
3.2: Molecular Orbital Theory
3.3: Valence Bond Theory
3.4: Hybrid Atomic Orbitals
3.5: Multiple Bonds formed between Hybridized Atoms
3.6: Resonance
3.7: Rules for Resonance Forms
3.8: Resonance Effects on Hybridization and Bonding
3.9: Hybridized Orbital Energy Diagrams
3.10: Key Terms
3.11: Summary
3.12: Exercises

This page titled 3: Advanced Theories of Covalent Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

3.1: Introduction

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields. Both N_2 and O_2 have fairly similar Lewis structures that contain lone pairs of electrons.

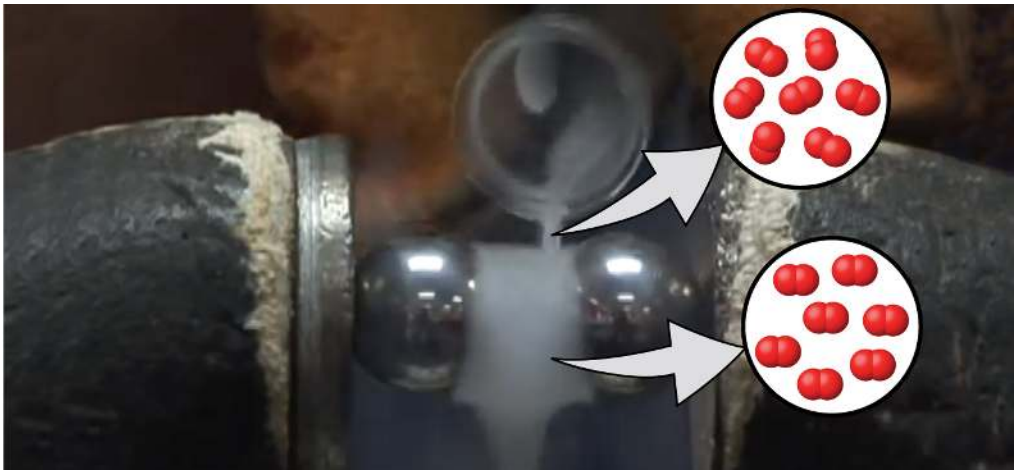


Figure 3.1.1: Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like N_2) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. (credit: modification of work by Jefferson Lab)

Yet oxygen demonstrates very different magnetic behavior than nitrogen. We can pour liquid nitrogen through a magnetic field with no visible interactions, while liquid oxygen (shown in Figure 3.1.1) is attracted to the magnet and floats in the magnetic field. We need to understand the additional concepts of valence bond theory, orbital hybridization, and molecular orbital theory to understand these observations.



This page titled 3.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

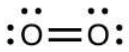
3.2: Molecular Orbital Theory

Learning Objectives

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

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called **paramagnetism**, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 3.2.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

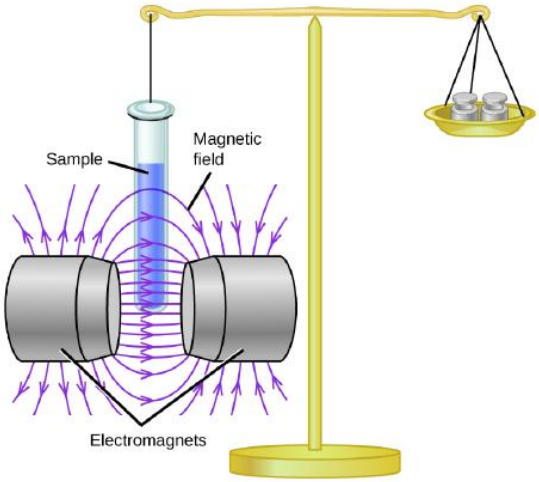


Figure 3.2.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

Link to Learning

Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more.

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 3.2.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals** (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (Figure 3.2.2). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

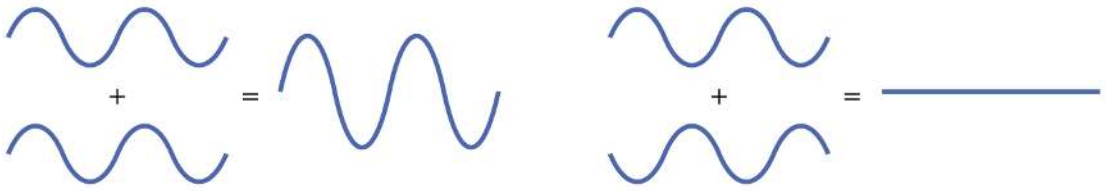


Figure 3.2.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure 3.2.3. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

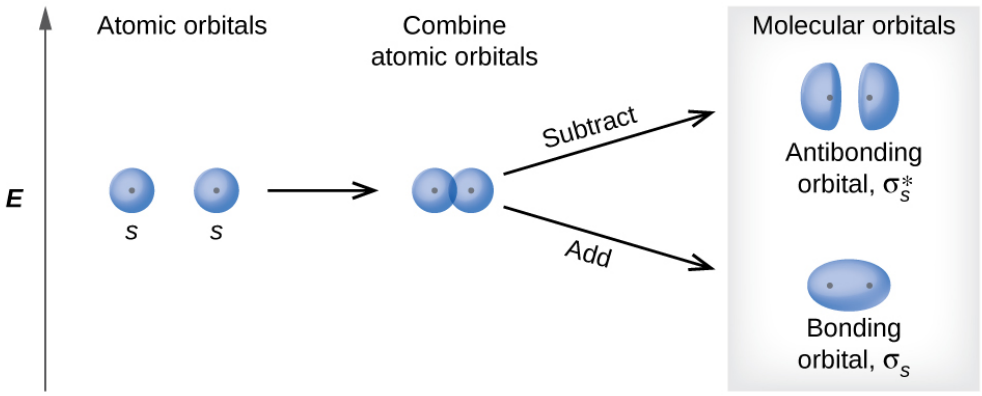


Figure 3.2.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two *s* atomic orbitals. The dots (·) indicate the locations of nuclei.

Link to Learning

You can watch animations visualizing the calculated atomic orbitals combining to form various molecular orbitals at the Orbitron website.

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure 3.2.4). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

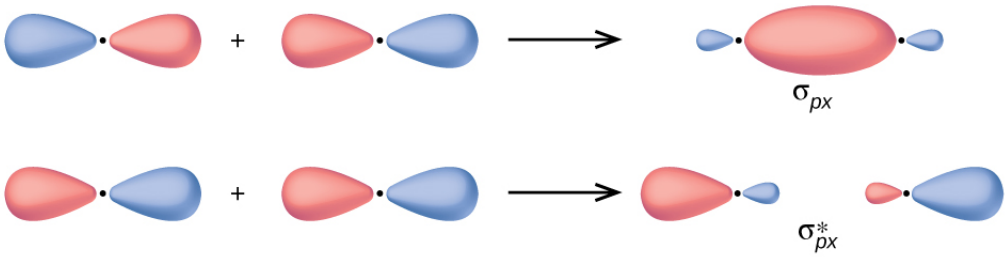


Figure 3.2.4: Combining wave functions of two *p* atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ^*_p

The side-by-side overlap of two *p* orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibonding molecular orbital**, as shown in Figure 3.2.5. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

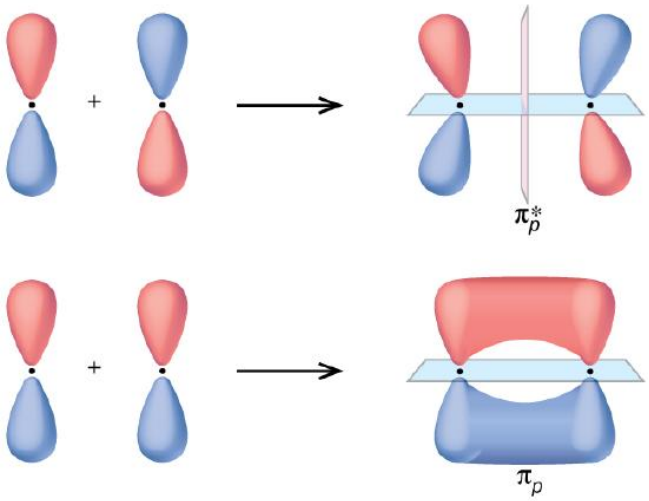
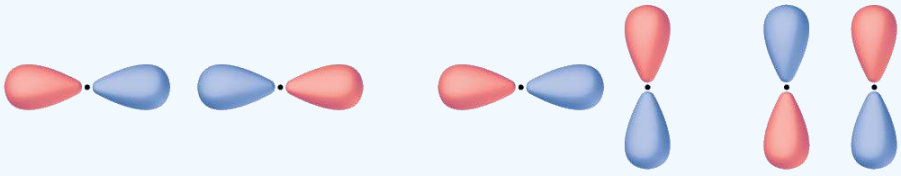


Figure 3.2.5: Side-by-side overlap of each two *p* orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

In the molecular orbitals of diatomic molecules, each atom also has two sets of *p* orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π* orbitals. The π_{py} and orbitals are oriented at right angles to the π_{pz} and π^*_{pz} orbitals. Except for their orientation, the \(π_{py}\) and \(π_{pz}\) orbitals are identical and have the same energy; they are **degenerate orbitals**. The π^*_{py} and π^*_{pz} antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic p orbitals in two atoms: σ_{px} and σ^*_{px}, π_{py} and π^*_{py}, π_{pz} and π^*_{pz}.

Example 3.2.1: Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.



$3p_x$ and $3p_x$ (a) $3p_x$ and $3p_y$ (b) $3p_y$ and $3p_y$ (c)

Solution

a. is an in-phase combination, resulting in a σ_{3p} orbital
b. will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.
c. is an out-of-phase combination, resulting in a \(\pi_{3 p}^*\) orbital.

Exercise 3.2.1

Label the molecular orbital shown as *σ* or π, bonding or antibonding and indicate where the node occurs.



Answer

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



Portrait of a Chemist: Walter Kohn: Nobel Laureate

Walter Kohn (Figure 3.2.6) is a theoretical physicist who studies the electronic structure of solids. His work combines the principles of quantum mechanics with advanced mathematical techniques. This technique, called density functional theory, makes it possible to compute properties of molecular orbitals, including their shape and energies. Kohn and mathematician John Pople were awarded the Nobel Prize in Chemistry in 1998 for their contributions to our understanding of electronic structure. Kohn also made significant contributions to the physics of semiconductors.

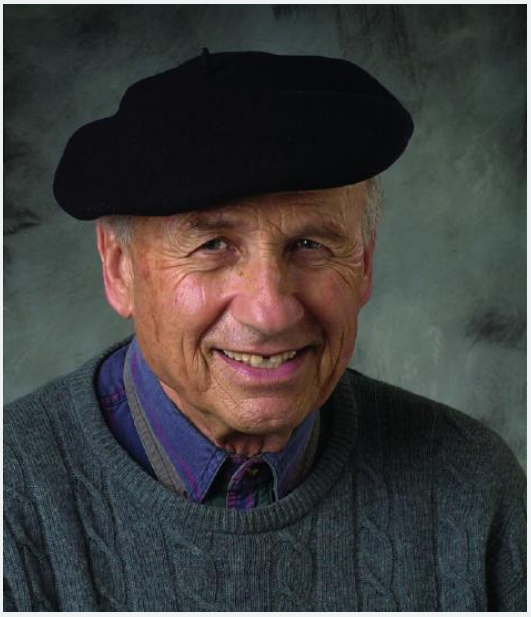


Figure 3.2.6: Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

Kohn's biography has been remarkable outside the realm of physical chemistry as well. He was born in Austria, and during World War II he was part of the Kindertransport program that rescued 10,000 children from the Nazi regime. His summer jobs included discovering gold deposits in Canada and helping Polaroid explain how its instant film worked. Dr. Kohn passed away in 2016 at the age of 93.

How Sciences Interconnect: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (see Figure 3.2.7). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

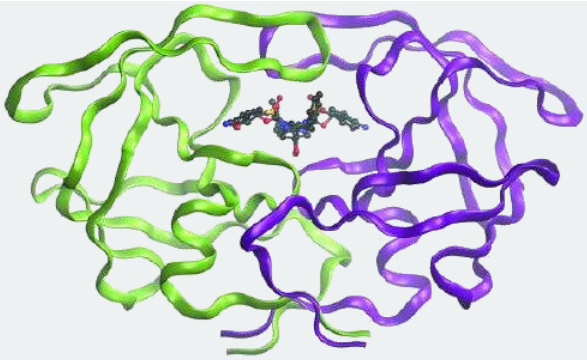


Figure 3.2.7: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 3.2.8). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 3.2.8). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+) would have the molecular electron configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

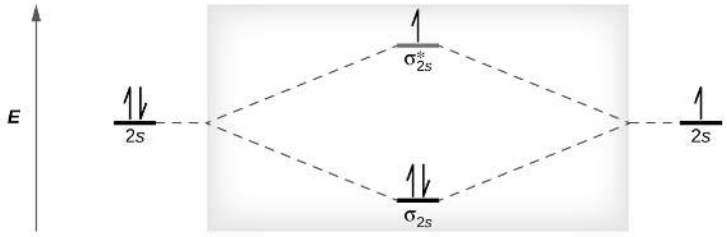


Figure 3.2.8: This is the molecular orbital diagram for the homonuclear diatomic showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing

(antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order } = \frac{(\text{number of bonding electrons }) - (\text{ number of antibonding electrons })}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases (Table 8.1). If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1*s* atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ1s bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 3.2.9) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

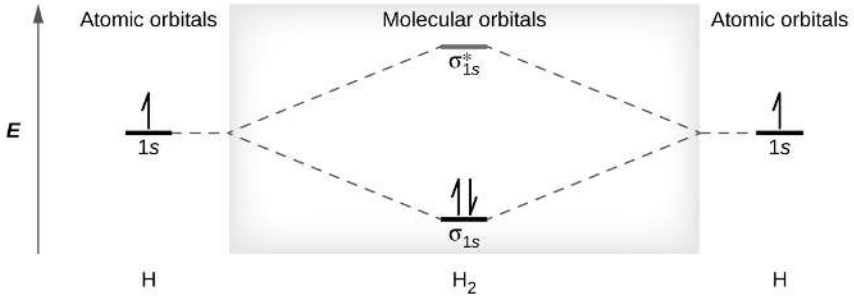


Figure 3.2.9: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1*s* orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

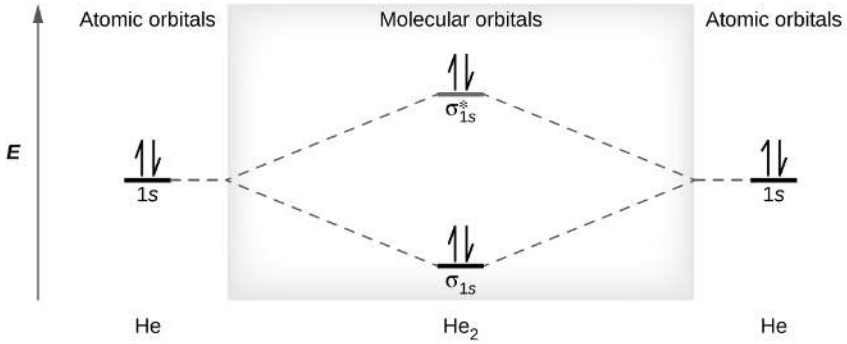


Figure 3.2.10: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table 3.2.2).

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund's rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure 3.2.11. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

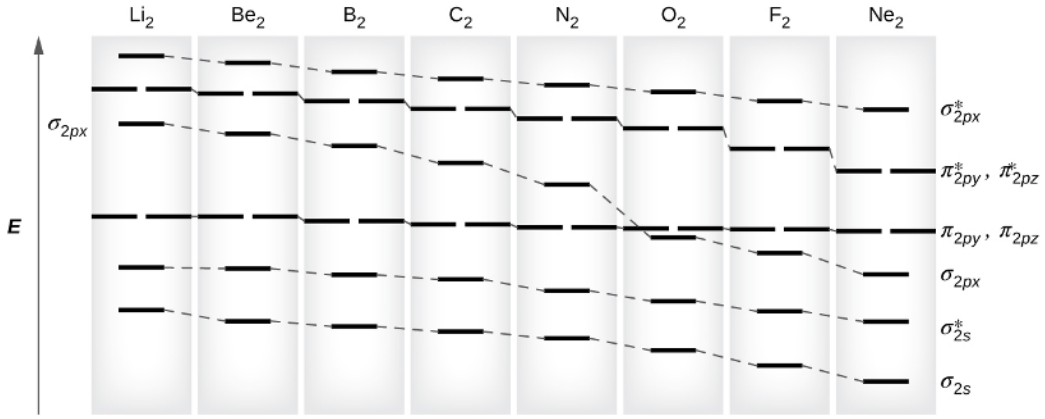


Figure 3.2.11: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes due to mixing.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure 3.2.12). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.

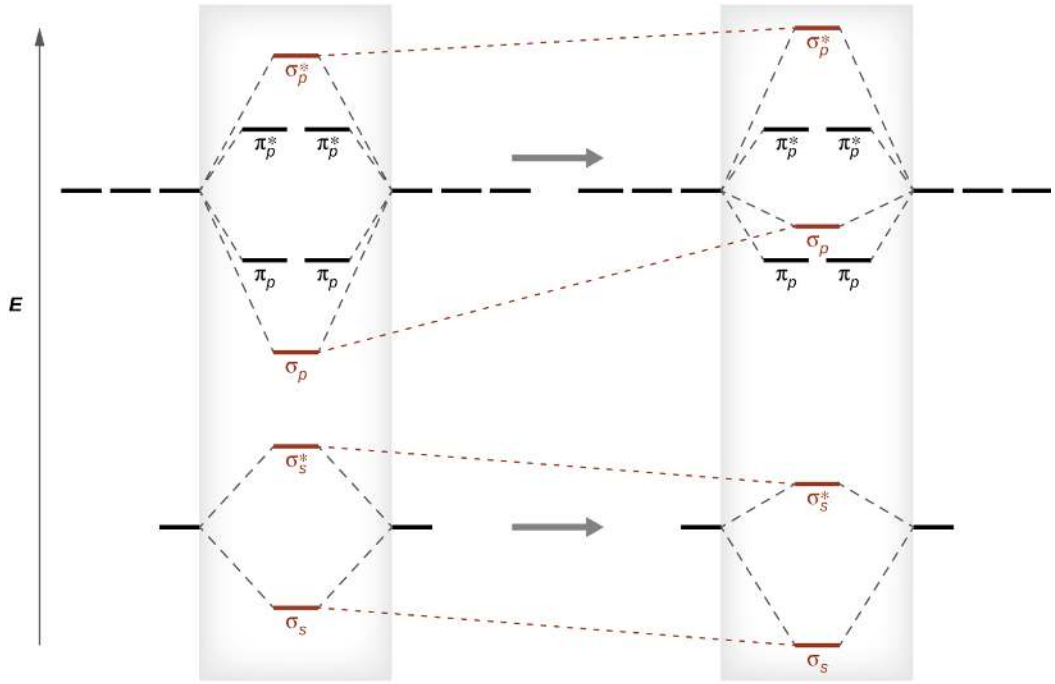


Figure 3.2.12: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the π_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

s-p mixing occurs when *s* and *p* orbitals on each side of the diagram have similar energies. The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne_2 exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 3.2.11. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in Figure 3.2.11: , we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in Table 3.2.2, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

Table 3.2.2: Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\pi_{2pz})^2$	1
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\pi_{2pz})^4$	2
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\pi_{2pz})^4(\sigma_{2px})^2$	3
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\pi_{2pz})^4\left(\pi^*_{2py},\pi^*_{2pz}\right)^2$	2
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\pi_{2pz})^4\left(\pi^*_{2py},\pi^*_{2pz}\right)^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\pi_{2pz})^4\left(\pi^*_{2py},\pi^*_{2pz}\right)^4\left(\sigma^*_{2px}\right)^2$	0

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2*s* orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the

Li_2 molecule to be stable. The molecule is, in fact, present in appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 3.2.2 with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the $\left(\pi^*_{2py}, \pi^*_{2pz}\right)$ level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure 8.40). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

How Sciences Interconnect: Band Theory

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (see Figure 3.2.3). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When *N* valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, *N*/2 (filled) bonding orbitals and *N*/2 (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. Figure 3.2.13 shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

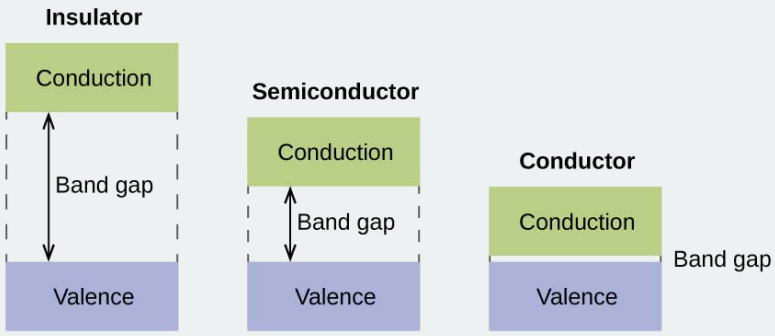


Figure 3.2.13: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is "easy" to overcome, so they are good conductors of electricity. In an insulator, the band gap is so "large" that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when "moderate" amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

Example 3.2.2: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 3.2.11. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 3.2.14

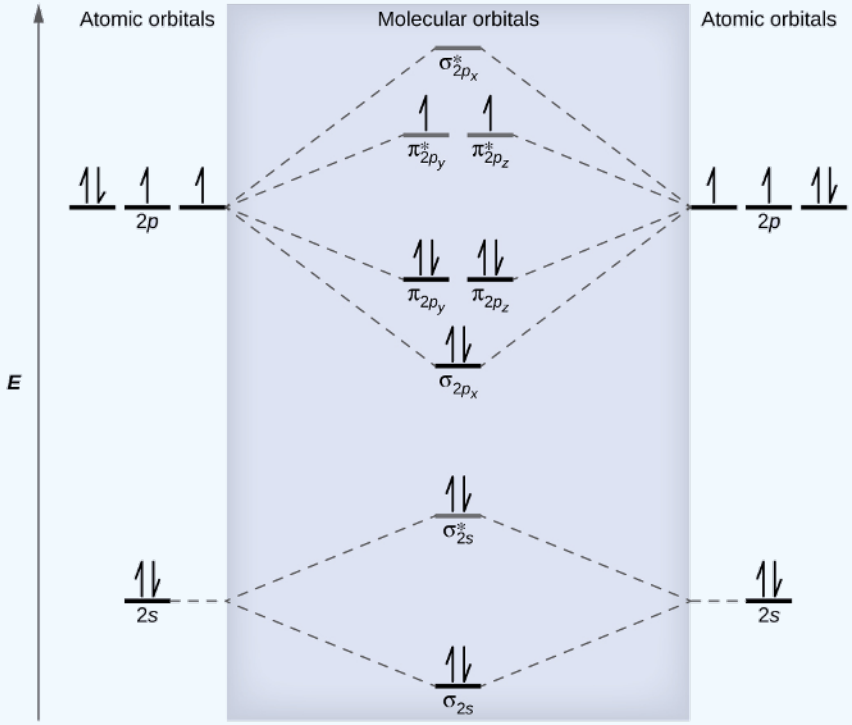


Figure 3.2.14: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

$$O_2 = \frac{(8-4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the (π_{2py}, π_{2pz})* molecular orbitals.

Exercise 3.2.2

The main component of air is N_2. From the molecular orbital diagram of N_2, predict its bond order and whether it is diamagnetic or paramagnetic.

Answer

N_2 has a bond order of 3 and is diamagnetic.

Example 3.2.3: Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable?

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σ_p orbital. The valence electron configuration for C_2 is $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py}, \pi_{2pz})^4$. Adding two more electrons to generate the C_2^{2-} anion will give a valence

electron configuration of $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\pi_{2pz})^4(\sigma_{2px})^2$. Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

? Exercise 3.2.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer

two, paramagnetic

Heteronuclear Diatomic Molecules

Diatomic molecules with two different nuclei are also common. The molecular orbital energy diagrams of these heteronuclear diatomic molecules will have different starting energies on either side of the diagram, corresponding to the atomic orbital energies of each atom. Some of these energies are shown in Table 3.2.1. The difference between the p and s orbital energies can give us insight into the energetic requirements of mixing, described above. O_2, which does not have signficant mixing, has an energy difference of 16.5 eV, whereas N_2, which does have significant mixing, has an energy difference of 12.4 eV. An energy difference of less than ~15 eV will lead to mixing in the heteronuclear diatomic molecular orbital diagram.

Table 3.2.1: Atomic Orbital Energies of Period 2 Elements

Element:	H	Li	Be	B	C	N	O	F
s orbital energy (eV)	-13.61	-5.39	-9.32	-14.05	-19.43	-25.56	-32.38	-40.17
p orbital energy (eV)				-8.30	-10.66	-13.18	-15.85	-18.65

? Exercise 3.2.4

Draw a molecular orbital diagram for the CN^- anion.

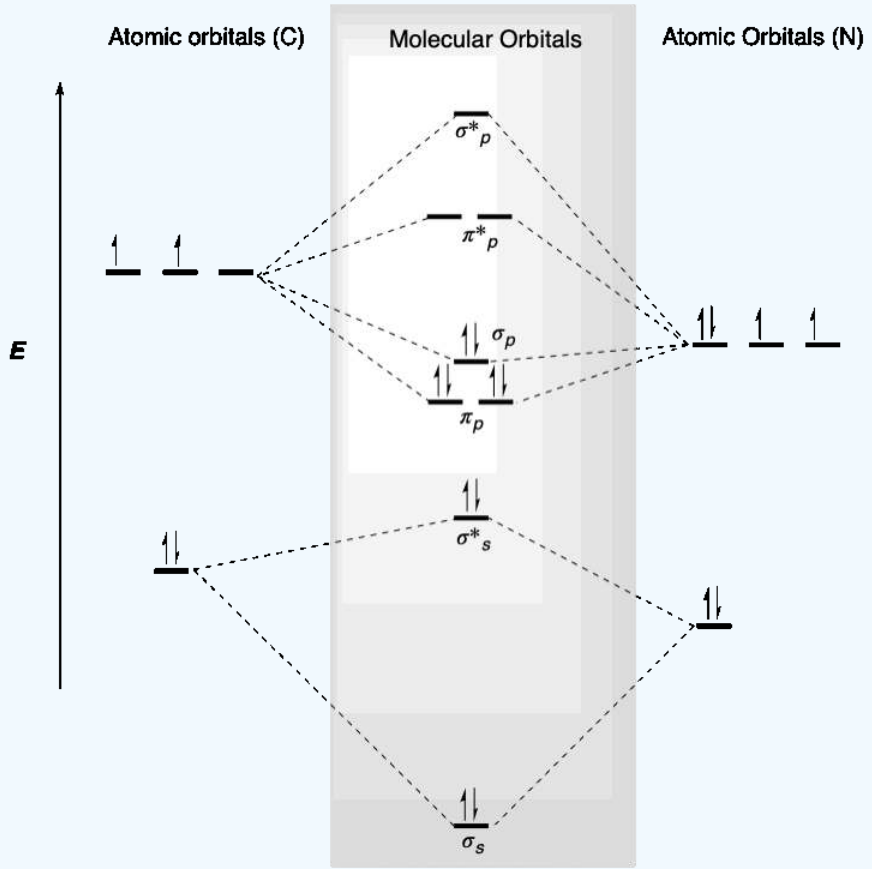
Solution

1. Electron count: C and N have 4 and 5 valence electrons, respectively, and there is an overall charge of -1. The total number of valence electrons is 10.

2. Starting energies of orbitals: We can check Table 3.2.1to find the starting energies of the s and p orbitals on C and N, and approximate them in our diagram, below.

3. Mixing or no mixing: The differences across the diagram are the following: s_C and p_N: 6.3 eV; s_N and p_C: 14.9 eV. As one (both, in this case) of these numbers is less than 15 eV, we can assume significant mixing in our orbital diagram, and the σ_p orbital will be raised above the π_p set.

4. All that is left is to draw the diagram, below.



Orbital Densities of Heteronuclear Diatomic Molecules

The drawings in Figure 3.2.4 (above) show how the orbital shapes change as they mix to become molecular orbitals from atomic orbitals. These orbital shapes are distorted when a molecule has nuclei with (1) different energy levels between each atom and (2) different electronegativities of each nucleus.

✔ Example 3.2.4: Shapes of atomic orbitals

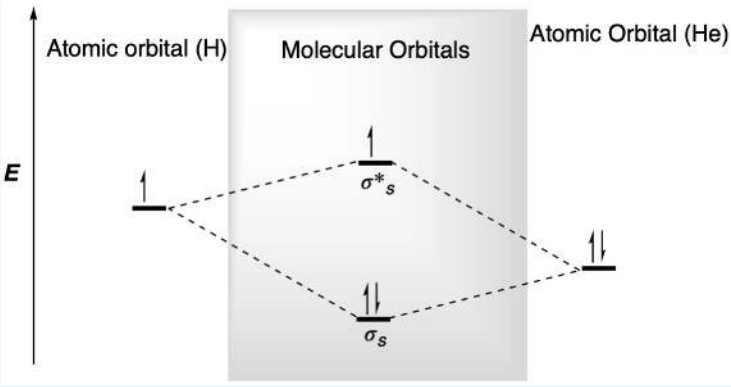
Draw the molecular orbital diagram of the molecule H-He.

(A) What is the bond order of H-He?

(B) Draw the shape of the bonding and antibonding orbitals, taking into account the electronegativities of each atom and the energy levels of the orbitals.

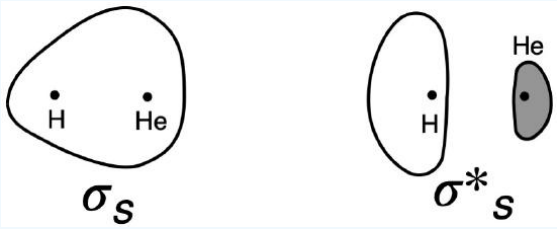
Solution

The helium (He) nucleus has more protons than hydrogen (H), yet both have only a 1s orbital as a valence orbital. Therefore, the starting 1s orbital for He should be lower in energy than the starting 1s orbital for H.



(A) Based on this diagram, the bond order is 1/2. This is because there are two bonding electrons and one antibonding electron.

(B) To draw the bonding and antibonding orbitals, we can start by looking at the bonding and antibonding orbitals shown in Figure 3.2.3. What is different about the heteronuclear orbitals is that He is more electronegative than H, and thus the bonding orbital is closer in energy to He, and the antibonding orbital is closer in energy to H. This affects the shape of the orbitals by biasing the molecular orbitals toward the orbitals they are closer in energy to.



The bonding orbital is closer in energy to He and thus it is biased toward the more electronegative helium. The antibonding orbital is biased toward H, in turn. Importantly, the shading of these orbitals is arbitrary. An answer with different shading would be equally correct, as long as the shading changes across the node in the σ* orbital.

Link to Learning

Creating molecular orbital diagrams for molecules with more than two atoms relies on the same basic ideas as the diatomic examples presented here. However, with more atoms, computers are required to calculate how the atomic orbitals combine. See three-dimensional drawings of the molecular orbitals for C_6H_6.

This page titled 3.2: Molecular Orbital Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

3.3: Valence Bond Theory

Learning Objectives

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

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

Table 3.3.1: Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Atomic Orbital Overlap

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an *s* orbital, a dumbbell shape for a *p* orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met: (1) an orbital on one atom overlaps an orbital on a second atom and (2) the single electrons in each orbital combine to form an electron pair. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure 5.2 illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between

the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure 5.2.

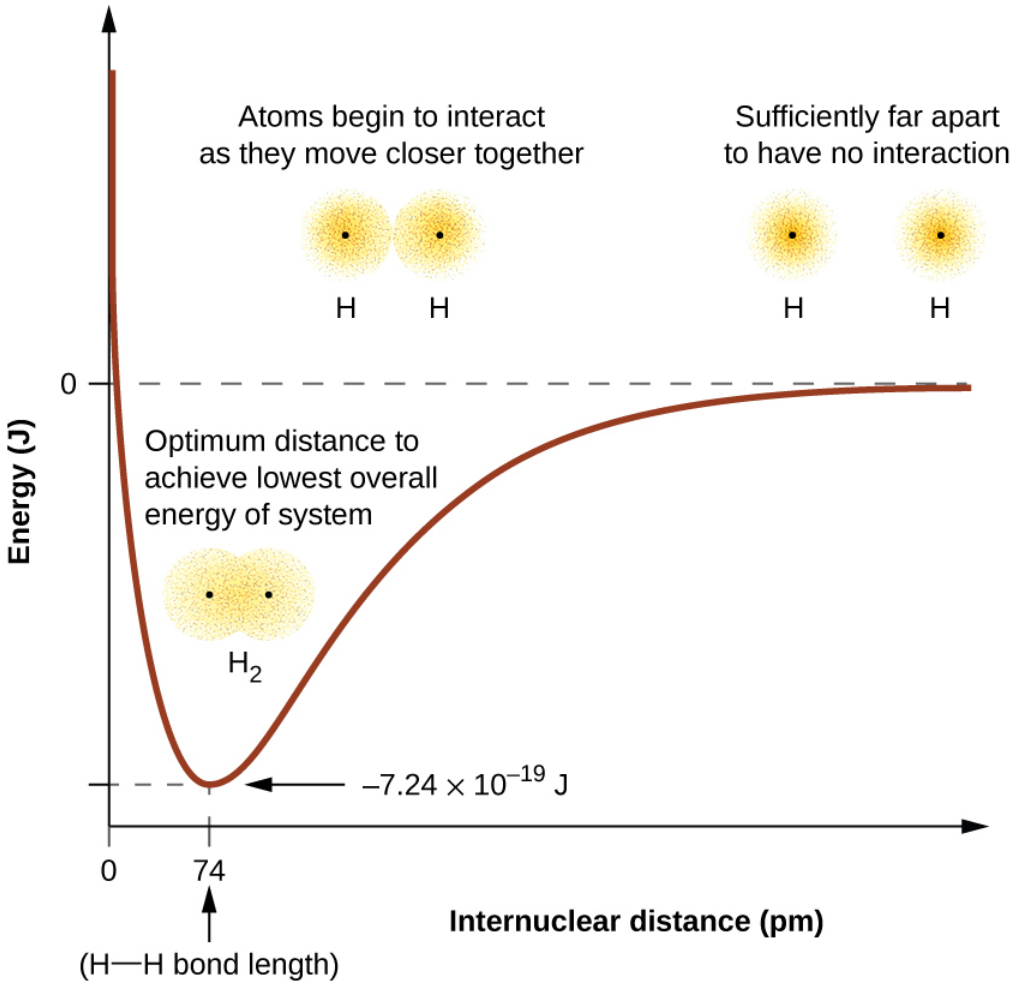


Figure 5.2 (a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two *s* orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 5.3 illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

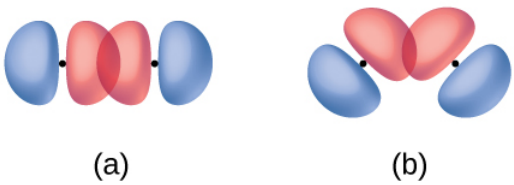


Figure 5.3 (a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two *s* orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure 5.4. A σ bond is a covalent bond in which the

electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

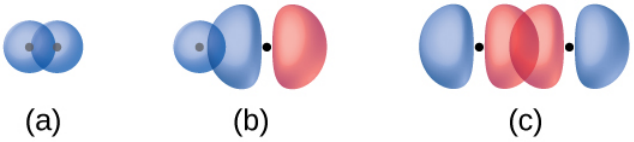


Figure 5.4 Sigma (σ) bonds form from the overlap of the following: (a) two *s* orbitals, (b) an *s* orbital and a *p* orbital, and (c) two *p* orbitals. The dots indicate the locations of the nuclei.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure 5.5. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

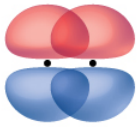
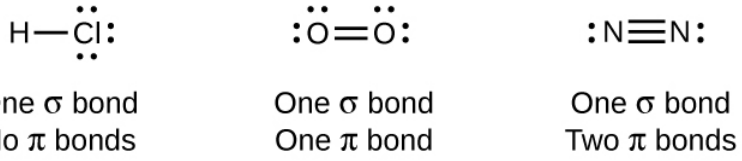


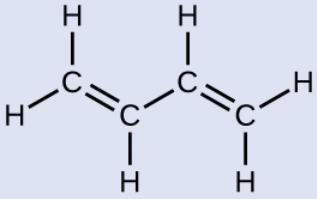
Figure 5.5 Pi (π) bonds form from the side-by-side overlap of two *p* orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures below suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.



Example 5.1

Counting σ and π Bonds



Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

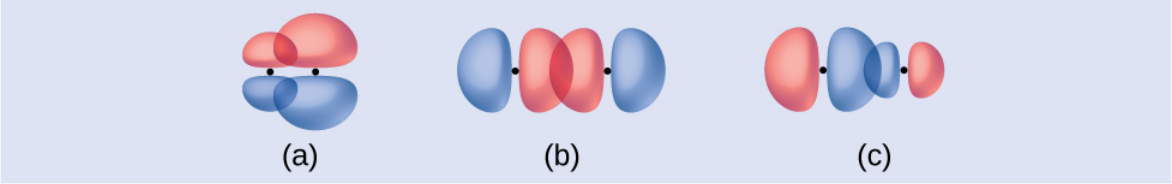
Check Your Learning

Identify each illustration as depicting a σ or π bond:

(a) side-by-side overlap of a 4*p* and a 2*p* orbital

(b) end-to-end overlap of a 4*p* and 4*p* orbital

(c) end-to-end overlap of a 4*p* and a 2*p* orbital



Answer:

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

Dipole Moments and Ionic Character

Now that we have seen the importance of understanding the connection between the location of electrons in atoms and the properties of elements, we can expand our understanding of the connection between atoms. This will be an introduction to more advanced aspects of the chemical bond, which is the very heart of chemistry itself. With the sole exception of the noble gases, atoms by themselves do not possess the most stable possible electron configuration. That is where the concept of chemical bonding comes into its own: atoms can attain a stable configuration by exchanging electrons with another atom, resulting in the formation of ions.

Ions, in turn, can associate by charge – simple Coulombic attraction – resulting in the formation of compounds we call ionic compounds. We will look at the ionic nature of bonds first, from a simple positive-negative attraction standpoint. Just as important is that some atoms bond by sharing rather than exchanging electrons; the sharing of electrons gives rise to the covalent bond. To add just one more dimension, some chemical species are neither completely ionic nor completely covalent; these species possess a permanent dipole, and are classified as polar.

In your introductory physics course, you will likely discuss the concept of Coulombic interactions in much more rigorous detail than we will do here. We are interested primarily in the differences in properties between species that arise from their relative covalent, ionic, or polar nature – not in a rigorous model of those properties. We are concerned with the connection between potential energy and force and the relative separation (or lack of separation) between charges. We begin by defining the electric or Coulomb force as the product of the charges divided by the square of the distance between those charges:

$$F = \frac{Q_1 Q_2}{d^2}$$

Here, *Q* is taken to be the fundamental constant of electron charge: one electron has a charge of 1.60218×10^{-19} C. (We will work exclusively in the SI system, so distances will be measured in meters (m)).

And as you may recall, energy is force times distance, so

$$E = \frac{Q_1 Q_2}{d}$$

To illustrate the trend in attractive force, we will consider first the attractive force between two ions of single charge separated by a distance of 2*d*:

$$F = \frac{(1)(-1)}{(2d)^2} = -\frac{1}{4d^2}$$

And then the attractive force between two ions of double charge separated by a distance *d*:

$$F = \frac{(2)(-2)}{(d)^2} = -\frac{4}{d^2}$$

The force of attraction increases with the charge and decreases with increased distance. If all matter were composed of ions that would be the end of the story, but it clearly is not. There are molecules for which the charge – either positive or negative – is permanently concentrated more on one atom than the other. Notice we say atom, because these compounds are not composed of ions but rather of atoms sharing electrons through covalent bonds.

Bond Dipole Moments

The concept of a bond dipole moment allows us to examine the partial separation of charge between atoms. It is a simple model when applied to diatomic molecules, which will be more than sufficient for our purposes. The dipole moment of a bond is defined as the charge times the distance – charge once again being measured in multiples of the charge on an electron, or coulombs. The distance will always be in meters. Because we are considering very small charges and distances, and because it is the relative separation of charge rather than the actual value for it that we are interested in, we will introduce a new unit called the Debye, named after the physical chemist Peter Debye:

$$1 \text{ Debye (D)} = 3.336 \times 10^{-30} \text{ C-m} \qquad \mu = Q \times d$$

The usefulness of the Debye unit will be shown by example:
For HCl, the bond dipole moment is known to be 1.08 D
For HI, the bond dipole moment is known to be 0.44 D

Comparing the two, we can see that HI is less polar than HCl, which is what we would expect based on electronegativity values.

We have now made a transition between the concept of an ionic compound and a partially ionic one. Of course, the partially ionic compound must also by definition be partially covalent.

Partial Ionic Character

The concept of the bond dipole moment helps bridge the concepts of ionic and covalent bonding. Because there is a separation of charge that is less complete than it is in an ionic bond, we can refer to polar bonds as being partially ionic in nature. In contrast to sodium chloride, hydrogen chloride shows partial charges (indicated with a delta notation) on the hydrogen and chlorine. As you would expect from the electronegativity values, hydrogen carries a partial positive charge, while chlorine carries a partial negative charge. Where do these charges come from?

It is easy to come up with the partial charges by comparing the actual dipole moments (which can be obtained experimentally, using spectroscopy) with the dipole expected in the limiting case (that is, if we were to consider the molecule ionic). The actual dipole moment is 1.03 D.

Example 5.2

Finding the Partial Ionic Character

What are the partial charges of an HCl molecule, whose bond length is 0.127 nm?

Solution

The bond dipole moment is $\left(1.60218 \times 10^{-19}\text{C}\right)\left(0.127 \times 10^{-9}\text{m}\right)$or $2.03 \times 10^{-29}\text{C-m}$. Converted to D, this is $\left(2.03 \times 10^{-29}\text{C-m}\right)\left(\frac{1\text{ Debye}}{3.336 \times 10^{-30}\text{C-m}}\right)$ or 6.09 D. Were HCl completely ionic, this would be its molecular dipole moment. To get the partial ionic character, we divide the experimentally measured bond moment by this limiting value: $\%\text{ionic character} = \frac{\mu_{\text{exp}}}{\mu_{\text{lim}}} \times 100\% = \frac{(1.03\quad \text{D}}{(6.09\quad \text{D})} \times 100\% = 17\%$. This means the bond is about 17% ionic – or, put another way, the positive charge in H is +0.17 and the partial negative charge on chlorine, –0.17.

Check Your Learning

Repeat the calculation for HI, which has a dipole moment of 0.42 D and a bond length of 0.161 nm.

Answer: Calculated 7.73, percent 5.43

What does the result suggest about the relative polarity of the HI bond vs. that of the HCl bond? Does the calculated dipole and percent ionic character reconcile with the difference in electronegativity between Cl and I?

The electron configuration of an atom or ion is key to understanding the chemical behavior of an element. The atoms that make up the element combine in various ways, ranging from the mostly ionic (NaCl) to the partially ionic (HCl) to what we will call purely covalent. At the most fundamental level, all chemical bonds involve electrons, and a significant percentage of chemical and physical properties can be explained by considering the location and separation of charge in a species. By understanding the structure of matter at the atomic level, we can begin to build an understanding of the behavior of matter at both the microscopic and macroscopic levels.

An understanding of dipoles and partial ionic character is fundamental to understanding the interactions between particles, which we will examine in the chapter on liquids and solids. These intermolecular forces become important in the liquid and solid states of matter.

This page titled 3.3: Valence Bond Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

3.4: Hybrid Atomic Orbitals

Learning Objectives

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

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two 2*p* orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2*p* orbitals with the 1*s* orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure 3.4.1, because *p* orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

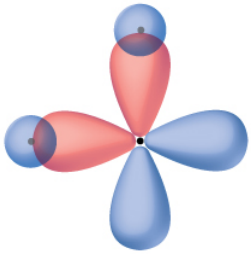


Figure 3.4.1: The hypothetical overlap of two of the 2*p* orbitals on an oxygen atom (red) with the 1*s* orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the 1*s* orbital of the hydrogen atoms with the 2*p* orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called **hybrid orbitals**. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 3.4.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

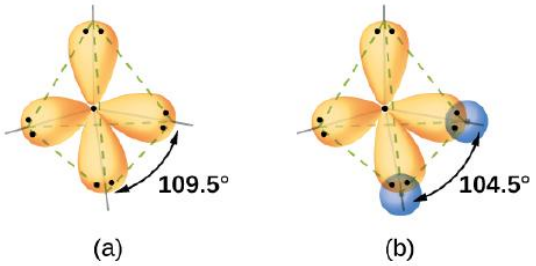


Figure 3.4.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1*s* orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.

3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent ***sp* hybrid orbitals** that are oriented in a linear geometry (Figure 3.4.3). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

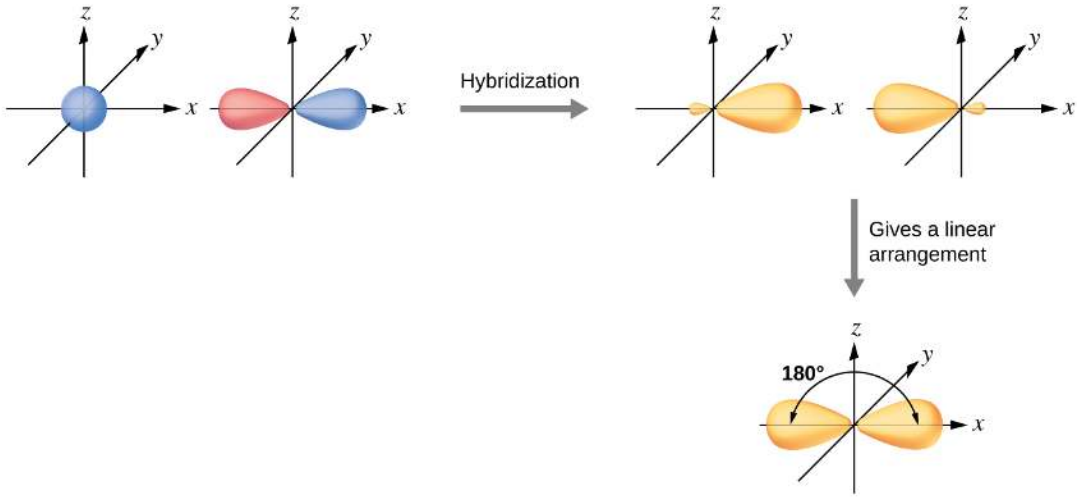


Figure 3.4.3: Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 3.4.4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

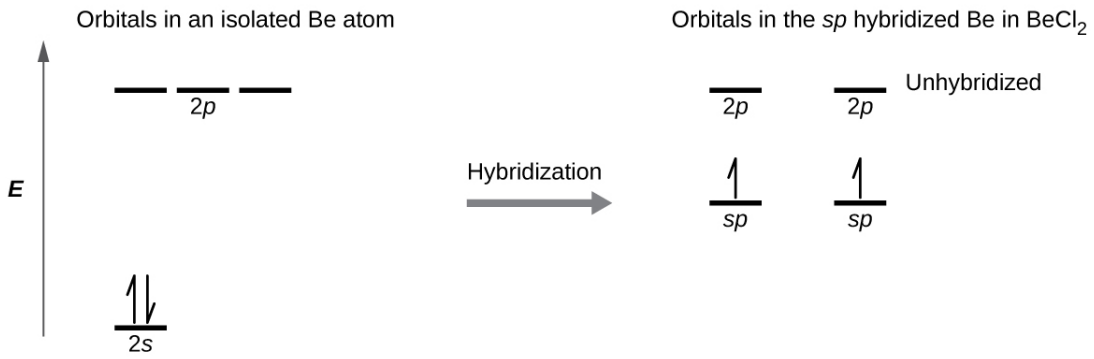


Figure 3.4.4: This orbital energy-level diagram shows the *sp* hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two *sp* hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3*p* orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

Link to Learning

Check out the University of Wisconsin-Oshkosh website to learn about visualizing hybrid orbitals in three dimensions.

sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three ***sp*^{2} hybrid orbitals** and one unhybridized *p* orbital. This arrangement results from sp^2 hybridization, the mixing of one *s* orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure 3.4.5).

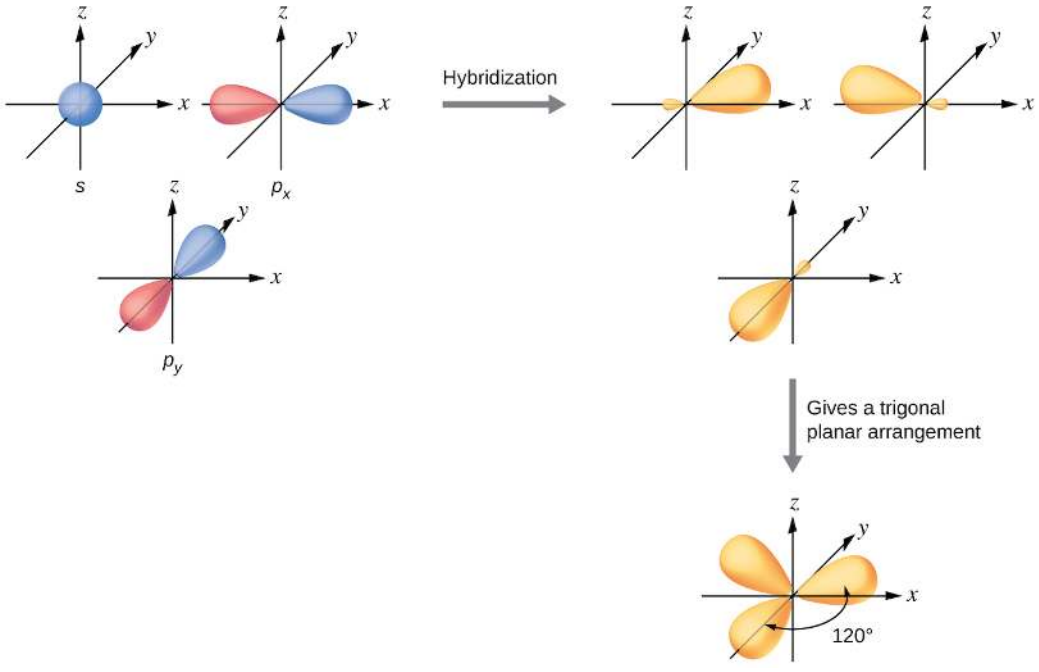


Figure 3.4.5: The hybridization of an *s* orbital (blue) and two *p* orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized *p* orbital is not shown here, but is located along the z axis. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

Although quantum mechanics yields the "plump" orbital lobes as depicted in Figure 3.4.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 3.4.6, to avoid obscuring other features of a given illustration. We will use these "thinner" representations whenever the true view is too crowded to easily visualize.

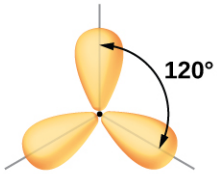


Figure 3.4.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 3.4.7). We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure 3.4.8. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

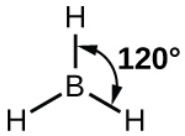


Figure 3.4.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.

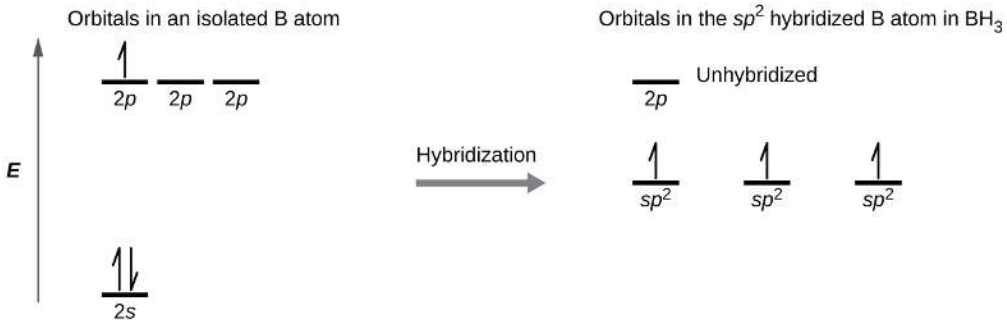


Figure 3.4.8: In an isolated B atom, there are one 2*s* and three 2*p* valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2*p* orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure 3.4.9), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.

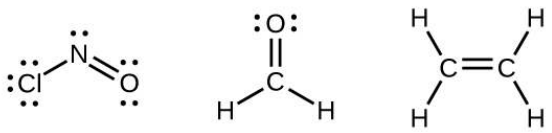


Figure 3.4.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four ***sp*^{3} hybrid orbitals**. The hybrids result from the mixing of one *s* orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure 3.4.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

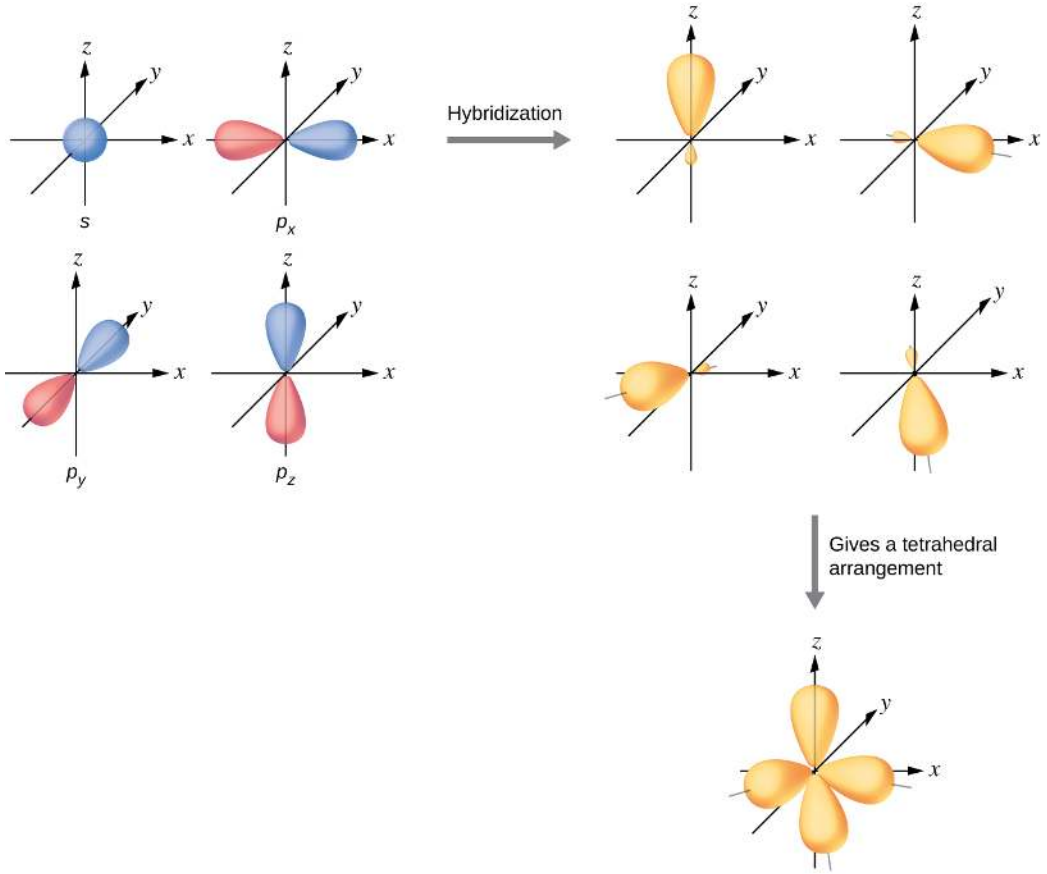


Figure 3.4.10: The hybridization of an *s* orbital (blue) and three *p* orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure 3.4.11. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

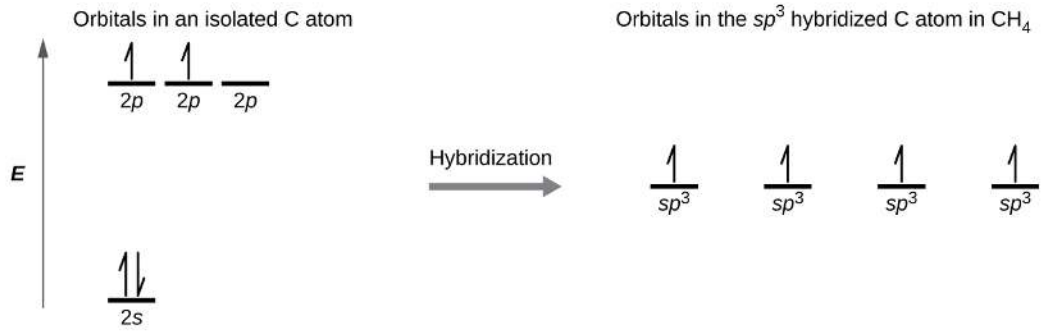


Figure 3.4.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the 1*s* orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 3.4.12). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each

of the remaining sp^3 hybrid orbitals overlaps with an *s* orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 3.4.12. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

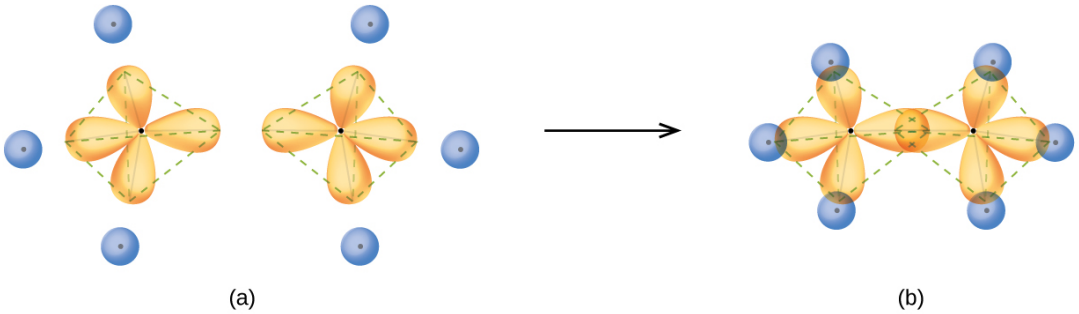


Figure 3.4.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and one of the *d* orbitals), which gives five ***sp*^{3}*d* hybrid orbitals**. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and two of the *d* orbitals in its valence shell), which gives six ***sp*^{3}*d*^{2} hybrid orbitals**. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells (that is, not those in the first or second period).

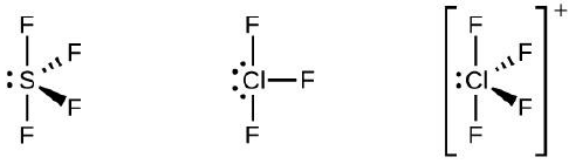


Figure 3.4.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3*s* orbital, the three 3*p* orbitals, and one of the 3*d* orbitals to form the set of five sp^3d hybrid orbitals (Figure 3.4.14) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in (The electrons on fluorine atoms are omitted for clarity.)

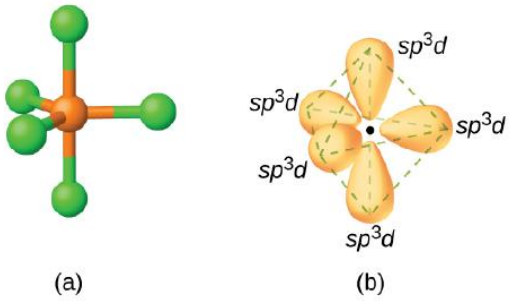


Figure 3.4.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3*s* orbital, the three 3*p* orbitals, and two of the 3*d* orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in the iodine atom in the interhalogens IF_5, and the xenon atom in XeF_4.

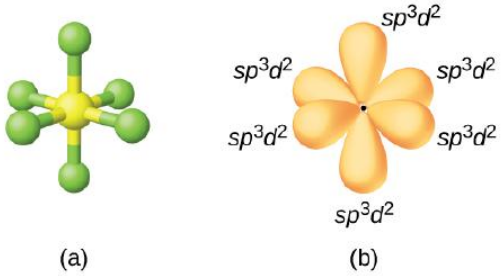


Figure 3.4.15: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure 3.4.16. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 3.4.16 that corresponds to this geometry.

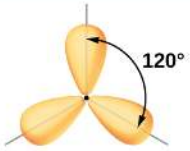
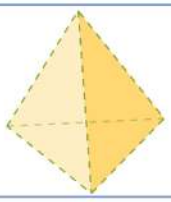
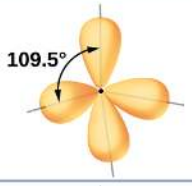
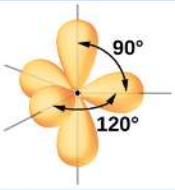
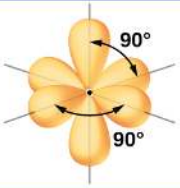
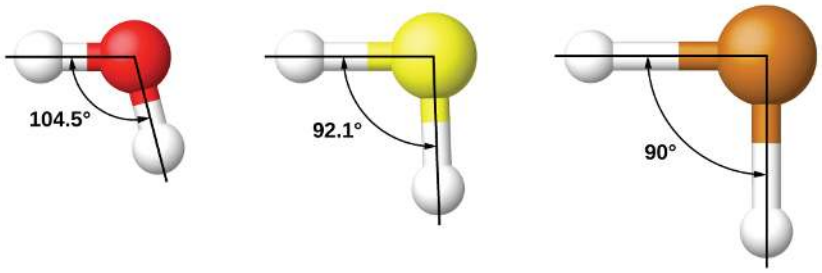
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure 3.4.16: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the 5*p* orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

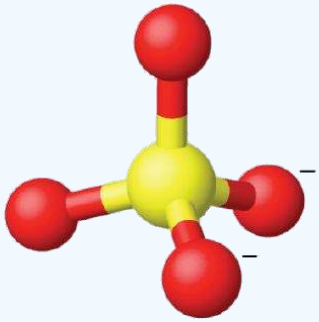


Example 3.4.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion,

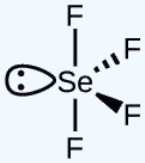
Solution

The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3.



Exercise 3.4.1

What is the hybridization of the selenium atom in SeF_4?



Answer

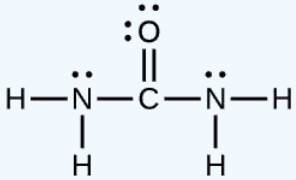
The selenium atom is sp^3d hybridized.

Example 3.4.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of the carbon atom in urea?

Solution

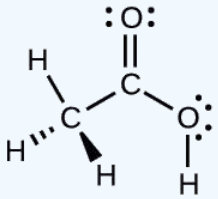
The Lewis structure of urea is



The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 3.4.16), which is the hybridization of the carbon atom in urea.

Exercise 3.4.1

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



Answer

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

Footnotes

- 1Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

This page titled 3.4: Hybrid Atomic Orbitals is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **8.2: Hybrid Atomic Orbitals** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

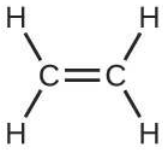
3.5: Multiple Bonds formed between Hybridized Atoms

Learning Objectives

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

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π-bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the 2*p* orbitals and the 2*s* orbital (Figure 3.5.1).

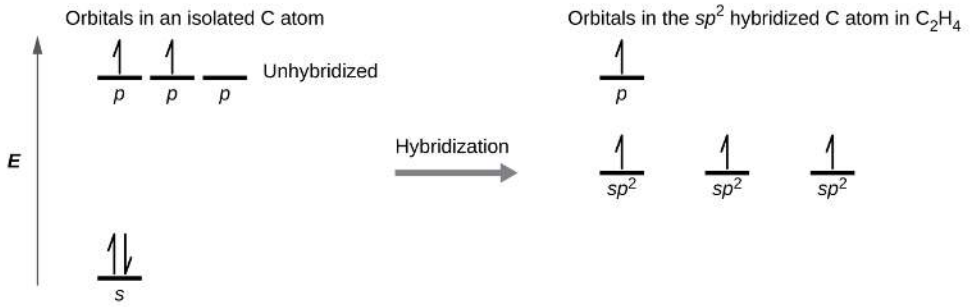


Figure 3.5.1: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the *p* orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.

These orbitals form the C–H single bonds and the σ bond in the Figure 3.5.2. The π bond in the C=C double bond results from the overlap of the third (remaining) 2p orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in Figure 3.5.2) is perpendicular to the plane of the sp2 hybrid orbitals. Thus the unhybridized 2p orbitals overlap in a side-by-side fashion, above and below the internuclear axis (Figure 3.5.2) and form a π bond.

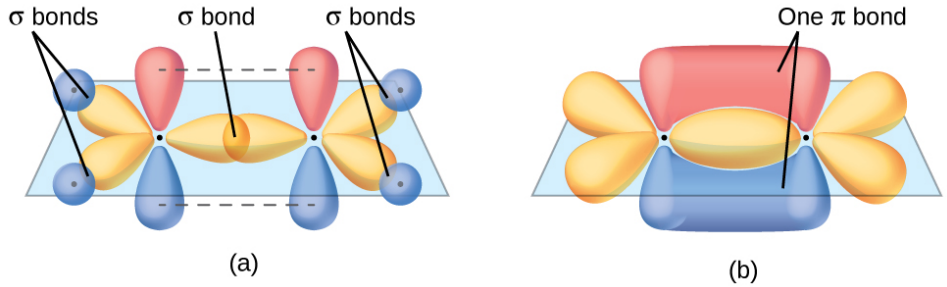


Figure 3.5.2: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with *s* orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the *p* orbitals would not be oriented to overlap efficiently to create the π bond. The planar

configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with *sp* hybrid orbitals, two unhybridized *p* orbitals remain on the atom (Figure 3.5.3). We find this situation in acetylene, $\mathrm{H-C\equiv C-H}$ (Figure 3.5.4), The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

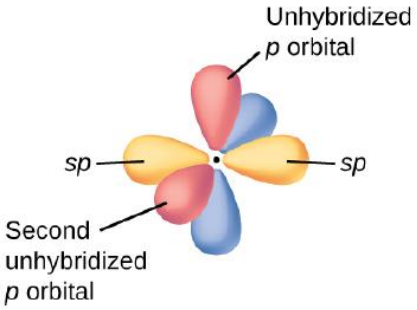


Figure 3.5.3: Diagram of the two linear *sp* hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized *p* orbitals at perpendicular angles. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

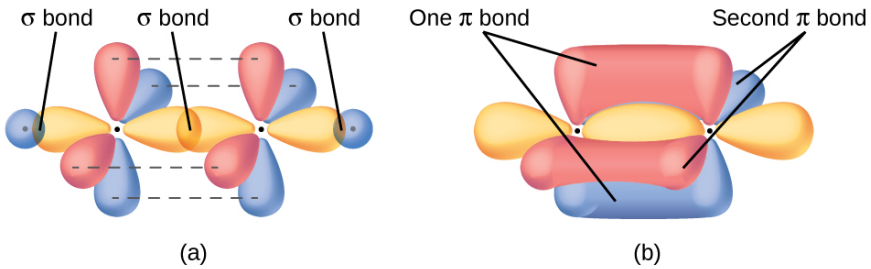


Figure 3.5.4: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure 3.5.5). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)

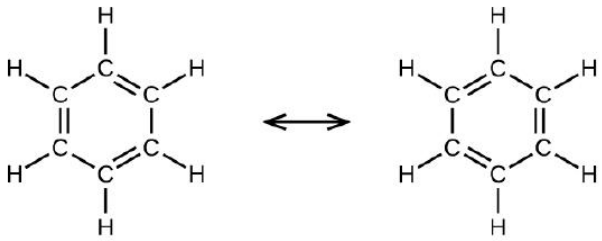


Figure 3.5.5: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of *p* orbitals or the other, but rather delocalized throughout the molecule.

Example 3.5.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2?

Solution

The resonance structures of SO_2 are



The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

In Chapter 3.9 we will discuss the hybridization of the oxygen atoms in SO_2.

Exercise 3.5.1

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer

sp^2

This page titled 3.5: Multiple Bonds formed between Hybridized Atoms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

3.6: Resonance

Objective

After completing this section, you should be able to

- draw resonance forms for molecules and ions.

Key Terms

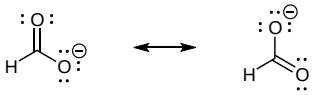
Make certain that you can define, and use in context, the key term below.

- resonance form
- delocalization

Resonance Delocalization

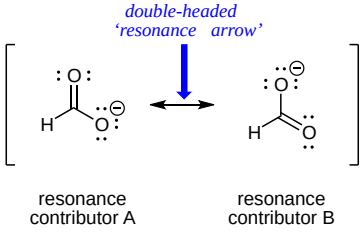
Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. **Resonance** is a way of describing **delocalized** electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance contributors or canonical forms). Resonance contributors involve the 'imaginary movement' of pi-bonded electrons or of lone-pair electrons that are adjacent to pi bonds. Note, sigma bonds cannot be broken during resonance – if you show a sigma bond forming or breaking, you are showing a chemical reaction taking place. Likewise, the positions of atoms in the molecule **cannot change** between resonance contributors.

When looking at the structure of the molecule, formate, we see that there are two equivalent structures possible. Which one is correct? There are two simple answers to this question: 'both' and 'neither one'. Both ways of drawing the molecule are equally acceptable approximations of the bonding picture for the molecule, but neither one, by itself, is an accurate picture of the delocalized pi bonds. The two alternative drawings, however, when considered together, give a much more accurate picture than either one on its own. This is because they imply, together, that the carbon-carbon bonds are not double bonds, not single bonds, but about halfway in between.



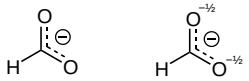
Formate Ion Structures are Equivalent in Energy

When it is possible to draw more than one valid structure for a compound or ion, we have identified **resonance contributors**: two or more different Lewis structures depicting the same molecule or ion that, when considered together, do a better job of approximating delocalized pi-bonding than any single structure. By convention, resonance contributors are linked by a double-headed arrow, and are sometimes enclosed by brackets:

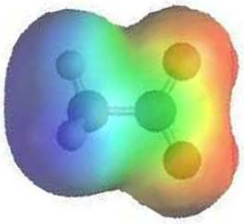


The depiction of formate using the two resonance contributors A and B in the figure above does *not* imply that the molecule at one moment looks like structure A, then at the next moment shifts to look like structure B. Rather, at all moments, the molecule is a combination, or **resonance hybrid** of both A and B. Each individual resonance contributor of the formate ion is drawn with one carbon-oxygen double bond (120 pm) and one carbon-oxygen single bond (135 pm), with a negative formal charge located on the single-bonded oxygen. However, the two carbon-oxygen bonds in formate are actually the same length (127 pm) which implies that neither resonance contributor is correct. Although there is an overall negative formal charge on the formate ion, it is shared equally

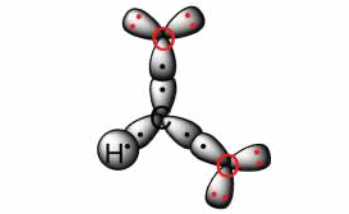
between the two oxygens. Therefore, the formate ion can be more accurately depicted by a *pair* of resonance contributors. Alternatively, a single structure can be used, with a dashed line depicting the resonance-delocalized pi bond and the negative charge located in between the two oxygens.



The electrostatic potential map of formate shows that there is an equal amount of electron density (shown in red) around each oxygen.

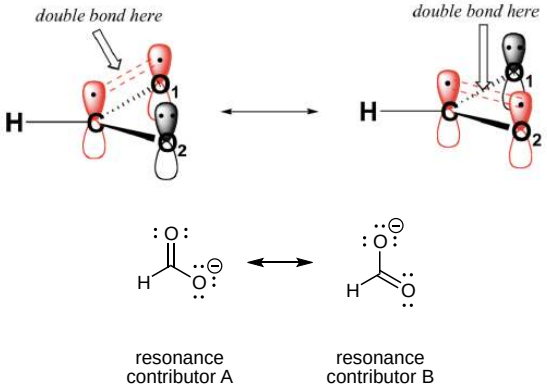


Valence bond theory can be used to develop a picture of the bonding in a carboxylate group. We know that the carbon must be sp^2-hybridized, (the bond angles are close to 120˚, and the molecule is planar), and we will treat both oxygens as being sp^2-hybridized as well. Both carbon-oxygen sigma bonds, then, are formed from the overlap of carbon sp^2 orbitals and oxygen sp^2 orbitals.



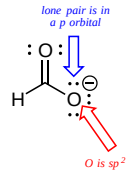
the σ-bonding framework of formate

In addition, the carbon and both oxygens each have an un-hybridized $2p_z$ orbital situated perpendicular to the plane of the sigma bonds. These three $2p_z$ orbitals are parallel to each other, and can overlap in a side-by-side fashion to form a delocalized pi bond.

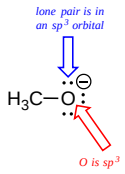


Overall, the situation is one of *three parallel, overlapping $2p_z$ orbitals sharing four delocalized pi electrons*. Because there is one more electron than there are $2p_z$ orbitals, the system has an overall charge of 1–. Resonance contributors are used to approximate overlapping $2p_z$ orbitals and delocalized pi electrons. Molecules with resonance are usually drawn showing only one resonance contributor for the sake of simplicity. However, identifying molecules with resonance is an important skill.

This example shows an important exception to the general rules for determining the hybridization of an atom. The oxygen with the negative charge appears to be sp^3 hybridized because it is surrounded by four electron groups. However, this representation of the oxygen atom is not correct because it is actually part of a resonance hybrid. A pair of lone pair of electrons on the negatively charged oxygen are not localized in an sp^3 orbital, rather, they are delocalized as part of a conjugated pi system. The stability gained though resonance is enough to cause the expected sp^3 to become sp^2. The sp^2 hybridization gives the oxygen a p orbital allowing it to participate in conjugation. As a general rule sp^3 hybridized atoms with lone pair electrons tend to become sp^2 hybridized when adjacent to a conjugated system.



oxygen is *conjugated*



oxygen is *not conjugated*

Example: Carbonate (CO_3^{2-})

Like formate, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the Lewis structures describing CO_3^{2-} has *three* equivalent representations.

1. Because carbon is the least electronegative element, we place it in the central position:

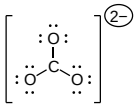


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the 2− charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

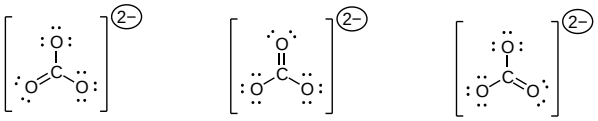


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the 2− charge:

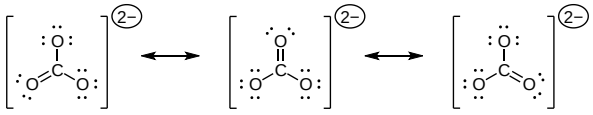


5. There are no electrons left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with formate, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



As the case for formate, the actual structure involves the formation of a molecular orbital from p_z orbitals centered on each atom and sitting above and below the plane of the CO_3^{2-} ion.

Example 2.4.1

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

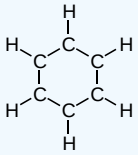
A Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C Draw the resonance structures for benzene.

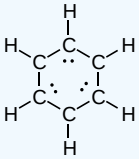
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



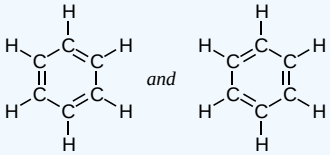
Each carbon atom in this structure has only 6 electrons and has a formal charge of 1+, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pair-wise on alternate carbon atoms, we obtain the following:

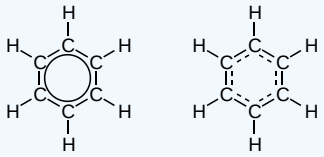


Three carbon atoms now have an octet configuration and a formal charge of 1−, while three carbon atoms have only 6 electrons and a formal charge of 1+. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:

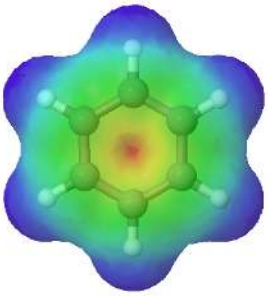


Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



benzene

This combination of *p* orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms. As can be seen in an electrostatic potential map of benzene, the electrons are distributed symmetrically around the ring.



? Exercise 3.6.1

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



Exercises

2.4 Resonance

2.4 Exercises

Draw the resonance structures for O_3

A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

Answer

1. We know that ozone has a V-shaped structure, so one O atom is central:



2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

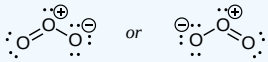


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. If the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures . The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:

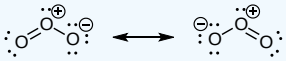
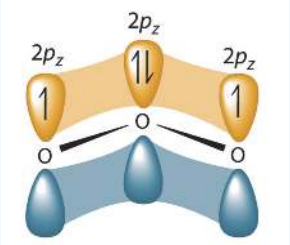


Figure 2.4.1).



https://chem.libretexts.org/@go/page/488577

The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms.In ozone, a molecular orbital extending over all three oxygen atoms is formed from three atom centered p_z orbitals. Similar molecular orbitals are found in every resonance structure.

3.6: Resonance is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Layne Morsch, Krista Cunningham, Tim Soderberg, & Tim Soderberg.

- **2.3: Resonance** by Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

3.7: Rules for Resonance Forms

Objectives

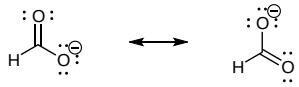
After completing this section, you should be able to

- use the concept of resonance to explain structural features of molecules and ions.
- understand the relationship between resonance and relative stability of molecules and ions.

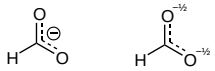
Rules for Drawing and Working with Resonance Contributors

Recognizing, drawing, and evaluating the relative stability of resonance contributors is essential to understanding organic reaction mechanisms. When learning to draw and interpret resonance structures, there are a few basic guidelines to help. .

1) There is ONLY ONE REAL STRUCTURE for each molecule or ion. This real structure (the **resonance hybrid**) takes its character from the average of all the individual **resonance contributors**. When looking at a resonance contributors, we are seeing the exact same molecule or ion depicted in different ways. Resonance hybrids are really a single, unchanging structure.



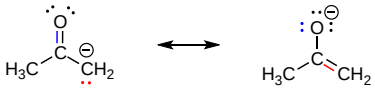
Major resonance contributors of the formate ion



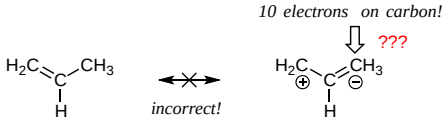
Representations of the formate resonance hybrid

2) The resonance hybrid is more stable than any individual resonance structures. Often, resonance structures represent the movement of a charge between two or more atoms. The charge is spread out amongst these atoms and therefore more stabilized. When looking at the picture above the resonance contributors represent the negative charge as being on one oxygen or the other. The resonance hybrid shows the negative charge being shared equally between two oxygens. In the resonance hybrid, the negative charge is spread out over a larger part of the molecule and is therefore more stable.

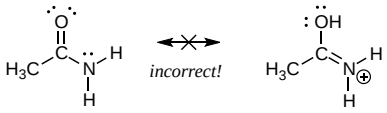
3) Resonance contributors do not have to be equivalent. Because of this, resonance structures do necessarily contribute equally to the resonance hybrid. The two resonance structures shown below are not equivalent because one show the negative charge on an oxygen while the other shows it on a carbon. Later, we will show that the contributor with the negative charge on the oxygen is the more stable of the two. Also, this means that the resonance hybrid will not be an exact mixture of the two structures.



4) All resonance contributors must be correct Lewis structures. Each atom should have a complete valence shell and be shown with correct formal charges. A carbocation (carbon with only 6 valence electrons) is the only allowed exception to the valence shell rules. The structure below is an invalid resonance structure even though it only shows the movement of a pi bond. The resulting structure contains a carbon with ten electrons, which violates the octet rule, making it invalid.



5) All resonance contributors must have the same molecular formula, the same number of electrons, and same net charge. The molecules in the figure below are not resonance structures of the same molecule because then have different molecular formulas (C_2H_5NO Vs. C_2H_6NO). Also, the two structures have different net charges (neutral Vs. positive).

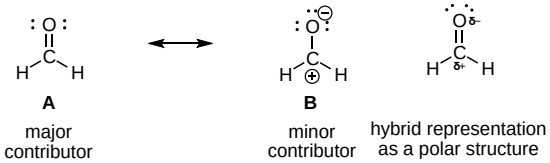


6) Resonance contributors only differ by the positions of pi bond and lone pair electrons. Sigma bonds are never broken or made, because of this atoms must maintain their same position. The molecules in the figure below are not resonance structures of the same molecule even though they have the same molecular formula (C_3H_6O). These molecules are considered structural isomers because their difference involves the breaking of a sigma bond and moving a hydrogen atom.



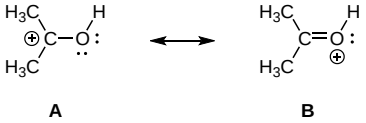
Major and Minor Resonance Contributors

As previously state the true structure of a resonance hybrid is the combination of all the possible resonance structures. If the resonance structures are equal in stability they the contribute equally to the structure of the hybrid. However, if the resonance structures have different stabilities they contribute to the hybrid's structure in proportions related to their relative stabilities. It can be said the the resonance hybrid's structure resembles the most stable resonance structure. Because of this it is important to be able to compare the stabilities of resonance structures. In the example below, structure **B** is much less important in terms of its contribution to the hybrid because it contains the violated octet of a carbocation. The relative stabilities of the two structures are so vastly different that molecules which contain a C=O bond are almost exclusively written in a form like structure **A**. However, as will learn in chapter 19, the positively charged carbon created by structure **B** will explain how the C=O bond will react with electron rich species.

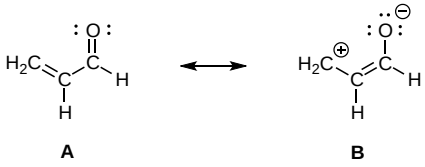


Rules for Estimating Stability of Resonance Structures

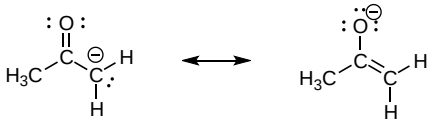
1. The resonance structures in which all atoms have complete valence shells is more stable. This means most atoms have a full octet. In the example below structure **A** has a carbon atom with a positive charge and therefore an incomplete octet. Based on this criterion, structure **A** is less stable and is a more minor contributor to the resonance hybrid than structure **B**.



2. The structures with the **least number of formal charges** is more stable. Based on this, structure **B** is less stable because is has two atoms with formal charges while structure **A** has none. Structure **A** would be the major resonance contributor.



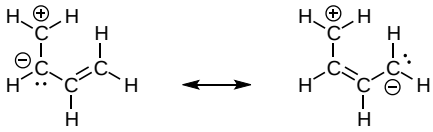
3. The structures with a **negative charge on the more electronegative atom** will be more stable. The difference between the two resonance structures is the placement of a negative charge. Structure **B** is the more stable and the major resonance contributor, because it places the negative charge on the more electronegative oxygen.



A **B**

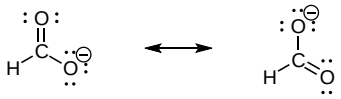
4. The structures with a **positive charges on the least electronegative atom** (most electropositive) is more stable.

5. The structures with the **least separation of formal charges** is more stable. The only difference between the two structures below are the relative positions of the positive and negative charges. In structure **A** the charges are closer together making it more stable.



A **B**

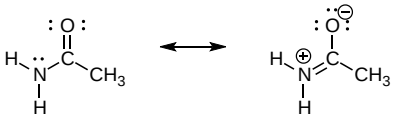
6. **Resonance forms that are equivalent have no difference in stability**. When looking at the two structures below no difference can be made using the rules listed above. This means the two structures are equivalent in stability and would make equal structural contributions to the resonance hybrid.



A **B**

Examples of major and minor contributors

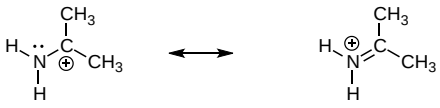
Example 1:



major contributor
(neutral structure)

minor contributor
(charge separation)

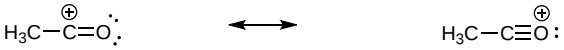
Example 2:



minor contributor
(Incomplete octet on carbon.)

major contributor
(All atoms have octets, even though there is a positive charge on nitrogen.)

Example 3:



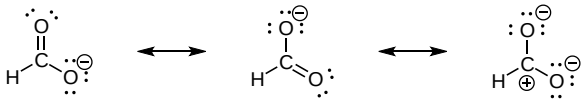
minor contributor
(Incomplete octet on carbon, but more important in terms of reactivity.)

major contributor
(All atoms have octets, even though there is a positive charge on oxygen.)

Carboxylate example

In the case of carboxylates, contributors **A** and **B** below are equivalent in terms of their relative contribution to the hybrid structure. However, there is also a third resonance contributor **C**, in which the carbon bears a positive formal charge (a carbocation) and both

oxygens are single-bonded and bear negative charges.



A B C

minor contributor
(separation of charge)

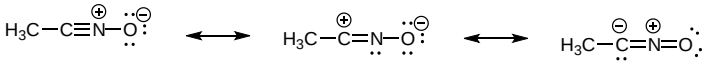
Structure **C** makes a less important contribution to the overall bonding picture of the group relative to **A** and **B**. How do we know that structure **C** is the 'minor' contributor? Apply the rules below

- The carbon in contributor **C** does not have an octet. In general, resonance contributors in which a carbon does not fulfill the octet rule are relatively less important. (rule #1)
- In structure **C**, there are only three bonds, compared to four in **A** and **B**. In general, a resonance structure with a lower number of total bonds is relatively less important. (rule #2)
- Structure **C** also has more formal charges than are present in **A** or **B**. In general, resonance contributors in which there is more/greater separation of charge are relatively less important. (rule #3)
- Structures **A** and **B** are equivalent and will be equal contributors to the resonance hybrid. (rule #5).
- The resonance contributor in which a negative formal charge is located on a more electronegative atom, usually oxygen or nitrogen, is more stable than one in which the negative charge is located on a less electronegative atom such as carbon. An example is in the upper left expression in the next figure. (rule #4)

Example with 3 resonance structures

Molecules with more than 2 resonance structures can also be considered using the rules listed above. Of the resonance structures listed below, structure **A** would be the most stable because all the non-hydrogen atoms have a full octet and the negative charge is on the more electronegative atom (oxygen). Structure **C** would be next in stability because all of the non-hydrogen atoms have full octets, though now the negative charge is on carbon rather than oxygen. Structure **B** would be the least stable of the three because it has the carbocation does not have an octet. Of the three, structure **A** would be the major resonance structure and would most resemble the structure of the true resonance hybrid. Structure **B** is considered a minor resonance contributor and would have very little effect on the structure of the resonance hybrid.

- **2.4: Rules for Resonance Forms** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.



A B C

3.7: Rules for Resonance Forms is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Steven Farmer, Dietmar Kennepohl, Krista Cunningham, Tim Soderberg, William Reusch, & William Reusch.

3.8: Resonance Effects on Hybridization and Bonding

Learning Objectives

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

- Identify delocalized molecular orbitals
- Explain the concept of delocalization and draw minor resonance contributors that affect hybridization
- Identify the hybridization of atoms with delocalized molecular orbitals

Delocalization of Molecular Orbitals

As described in Chapter 2.5, **resonance forms** of a molecule cannot completely describe the bonding in a molecule without taking into account each resonance structure and averaging these as a **resonance hybrid**. This phenomenon is not limited to bond order and charge distribution, and can be applied to molecular orbitals as well. ***Delocalized molecular orbitals*** are orbitals that are extended across multiple atoms rather than being constrained to one or two atoms, and thus molecules with resonance structures will have delocalized molecular orbitals.

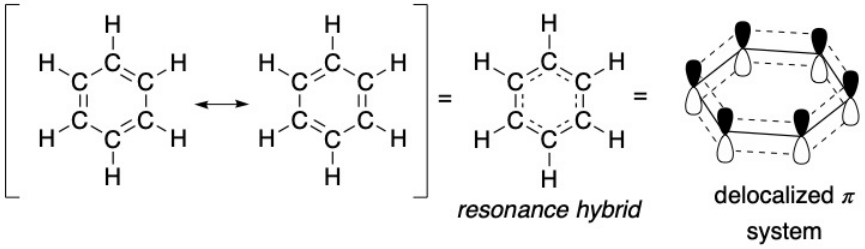


Figure 3.8.1: different visualizations of benzene.

Benzene has two major resonance structures with alternating double bonds (Figure 3.8.1). In the resonance hybrid (and in the actual molecule), each C-C bond is effectively 1.5 bonds, due to resonance. The p orbitals that make up each π bond are conserved in the resonance structures and resonance hybrid, as seen in the delocalized π system.

The hybridization of each carbon in the benzene ring is sp^2, and this hybridization is conserved in the resonance hybrid and delocalized π system that is made up of the unhybridized p orbitals.

Hybridization of Resonance Contributors

Returning to O_3 (ozone) from Chapter 3.6:

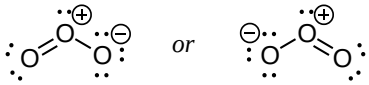


Figure 3.8.2: Two resonance contributors of Ozone

The terminal oxygen atoms on each resonance structure have a different number of regions of electron density. At first glance, the oxygen atoms would have different hybridizations as a result. However, the resonance hybrid is the true structure of the molecule, with a partial negative charge on each terminal oxygen and a full positive charge on the central oxygen.

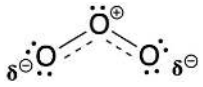


Figure 3.8.3: Ozone resonance Hybrid

The resonance hybrid (Figure 3.8.3) shows how the p orbitals on all three oxygen atoms form a *delocalized* molecular orbital. Thus, each oxygen is sp^2 hybridized, with the p orbitals forming a π system, and 5 lone pairs in sp^2 hybridized orbitals on the oxygen atoms.

This delocalization is favorable for the molecule, because the electrons in the p orbitals are spread out over more atoms. When possible, molecules will adopt hybridization arrangements to allow for delocalization of electrons.

An orbital picture of the resonance hybrid could be drawn as shown in Figure 3.8.4, with the p orbitals and π system shown in grey and the hybridized orbitals shown in blue (minor lobes of hybridized orbitals not shown for clarity). The lone pairs are in hybridized orbitals, and the π system has 4 electrons (not shown) spread out over three atoms. This delocalization of electrons stabilizes the molecule and encourages the sp^2 hybridization.

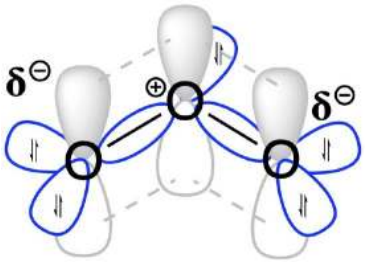


Figure 3.8.4: Delocalized molecular orbitals in Ozone.

Minor Resonance Contributors

While O_3 (above) has two equal resonance contributors, delocalization will occur when possible, even when this involves minor resonance contributors, as shown in Figure 3.8.5.

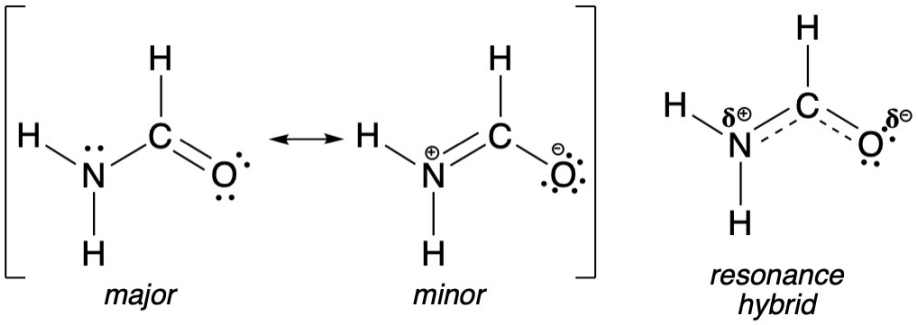


Figure 3.8.5: Major and Minor resonance forms of formamide, and its resonance hybrid.

The resulting hybridization of each atom in formamide will be in accordance with the resonance hybrid, which means that N, C, and O will each have an unhybridized p orbital as part of the delocalized molecular orbital. The hybridizations can be seen in Figure 3.8.6.

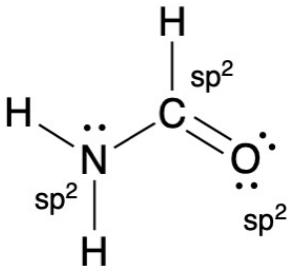


Figure 3.8.6: Hybridization of atoms in formamide due to resonance delocalization.

This page titled 3.8: Resonance Effects on Hybridization and Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Alexandra Strom.

- **7.4: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.9: Hybridized Orbital Energy Diagrams

Mixing Hybridized Orbitals and Formation of Antibonding orbitals

As shown in Section 3.4, the energy levels of hybridized atomic orbitals are a weighted average of the mixed atomic orbitals (Figure 3.9.1). When two hybridized atoms approach each other, the orbitals mix to form bonds. However, as with hybridization, mixing of orbitals results in the exact same number of mixed orbitals as there were originally. This means that for every bonding orbital between atoms, there is an antibonding orbital, which is not shown in the diagrams in Chapter 3.4, for the sake of simplicity. Bonding orbitals are lower in energy than the starting atomic orbitals, and the corresponding antibonding orbitals are higher in energy.

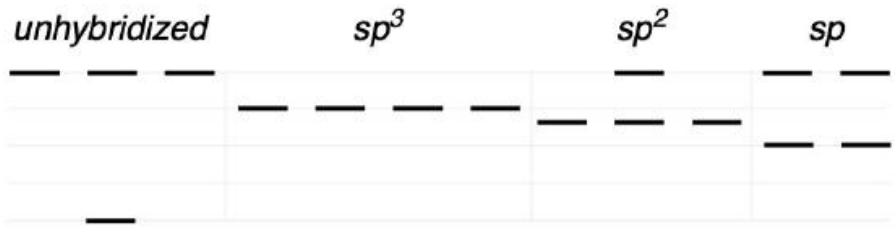


Figure 3.9.1 : orbital energies of hybridized orbitals.

Bonding interactions with a large amount of spatial overlap will be the strongest (e.g., σ bonds) and those with less spatial overlap will be weaker (e.g., π bonds). Each interaction between hybridized orbitals will create an in-phase bonding interaction and an out-of-phase antibonding interaction. For more on bonding, antibonding, and phases of orbitals, see Chapter 3.2: Molecular Orbital Theory.

Hybridized orbital energy levels will vary based on the number of s and p orbitals that are hybridized. For example, sp hybridized orbitals have 50% "s-character" and 50% "p-character" and thus their energy will be halfway between the starting s and p orbital energies, and thus lower in energy than an sp^2 orbital on the same element (Figure 3.9.1).

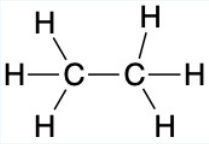
In the same way that we can use hybridized atoms to form bonds through overlapping hybridized orbitals in Chapter 3.4 and 3.5, we can form bonds between the orbitals using energy diagrams to gain insight into the energy levels of different bonds.

Example 3.9.1 : Hybridized orbital energy diagram of ethane (C_2H_6)

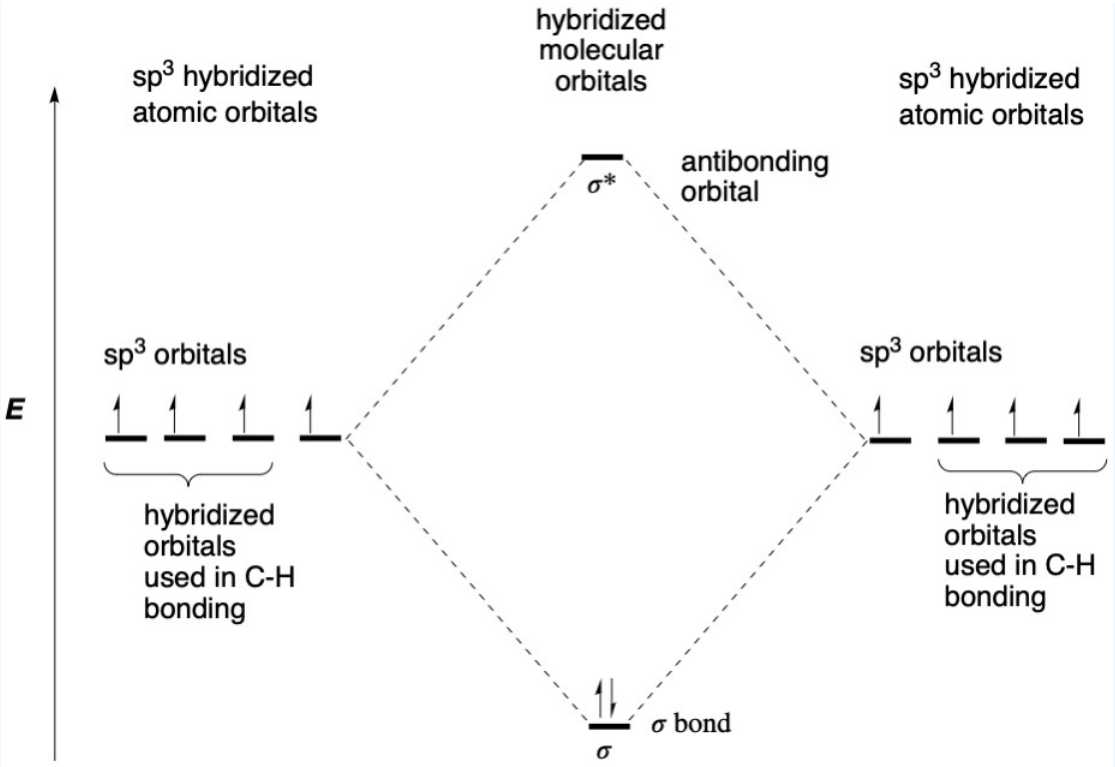
Draw the hybridized orbital energy diagram of the C-C bond in ethane (C_2H_6). What is the lowest energy unoccupied orbital in this diagram?

Solution

1. The Lewis structure of ethane shows a single bond between the two carbons and single bonds with the six Hs.



2. The carbons in ethene are both sp3 hybridized, which gives us four sp^3 orbitals. One of the hybridized orbitals on each carbon is involved in σ bonding (stronger interaction, lower energy bonding orbital). These two orbitals interact to form the bonding interaction, as well as an antibonding interaction. The remaining hybridized orbitals are involved in C-H bonds. There are no lone pairs or π bonds.



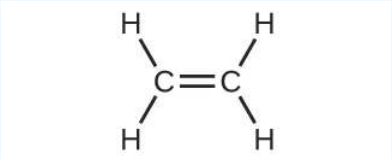
Example 3.9.1 shows how the starting hybridized *atomic* orbitals from Figure 3.9.1 mix to form bonding interactions and antibonding interactions in *molecular* orbitals.

Example 3.9.2 : Hybridized orbital energy diagram of ethene (C_2H_4)

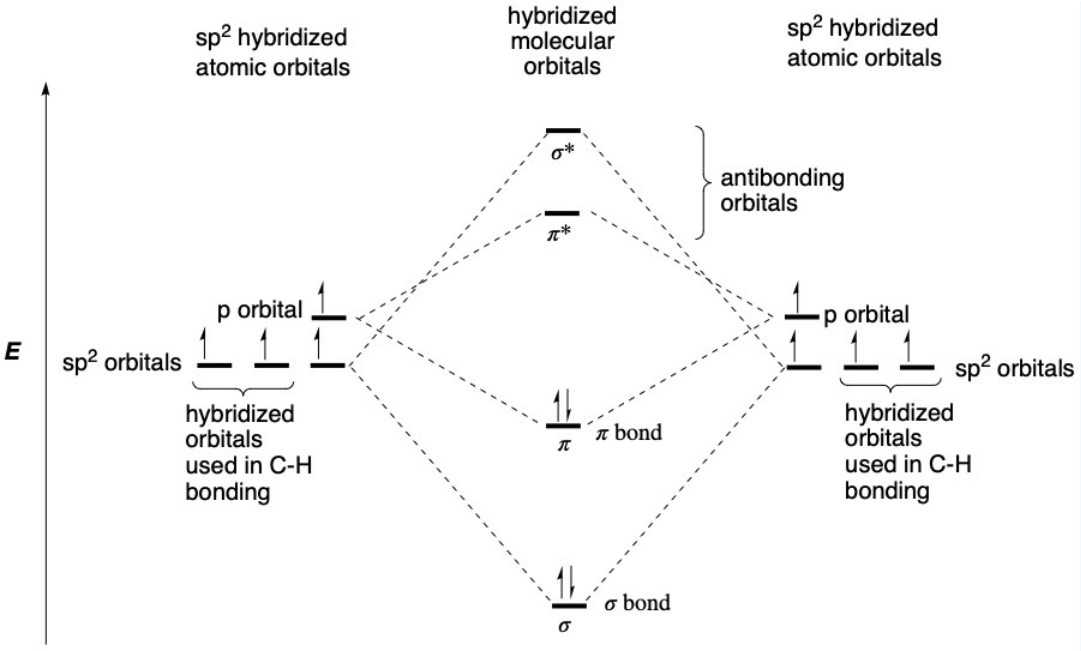
Draw the hybridized orbital energy diagram of the C-C bond in ethene (C_2H_4). What is the lowest energy unoccupied orbital in this diagram?

Solution

1. The Lewis structure of ethene shows a double bond between the two carbons and single bonds with the four Hs.



2. The carbons in ethene are both sp^2 hybridized, which gives us one un-hybridized p orbital on each carbon atom and three sp^2 orbitals. One of the hybridized orbitals on each carbon is involved in σ bonding (stronger interaction, lower energy bonding orbital) and the un-hybridized p orbital on each carbon is involved in π bonding (weaker interaction). These interactions can be shown in the following diagram:



Example 3.9.2 shows how the starting hybridized *atomic* orbitals from Figure 3.9.1 mix to form bonding interactions and antibonding interactions in *molecular* orbitals. These molecular orbitals have different energies based on the overlap between the starting hybridized orbitals. The σ bond is formed between two sp^2 hybridized orbitals, which point towards each other, as shown in Chapter 3.5. This strong overlap in atomic orbitals results in a lower energy and more stable bonding orbital. The two p orbitals have less spatial overlap, and thus the bond is less strong between these atomic orbitals, and the corresponding bonding orbital is higher in energy. The stabilization gained in each bonding interaction is proportional to the destabilization of the antibonding orbitals.

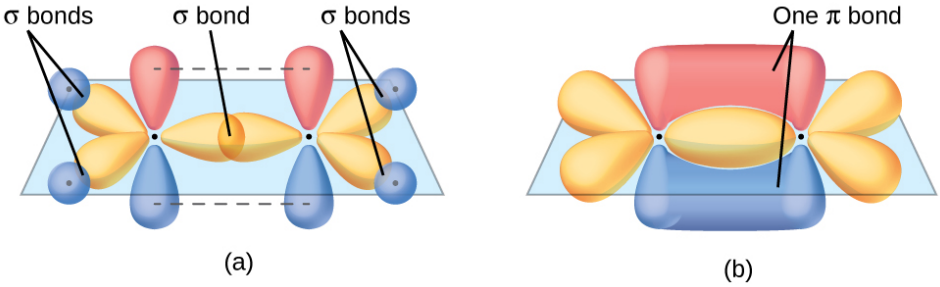


Figure 3.9.2 : In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with *s* orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

? Exercise 3.9.2

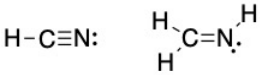
Using hybridized orbital energy diagrams for bonding in HCN and $H_2C{=}NH$,

A) What are the hybridizations of each C and N?

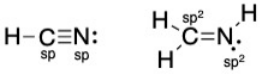
B) Which lone pair is highest in energy between these two molecules?

Answer

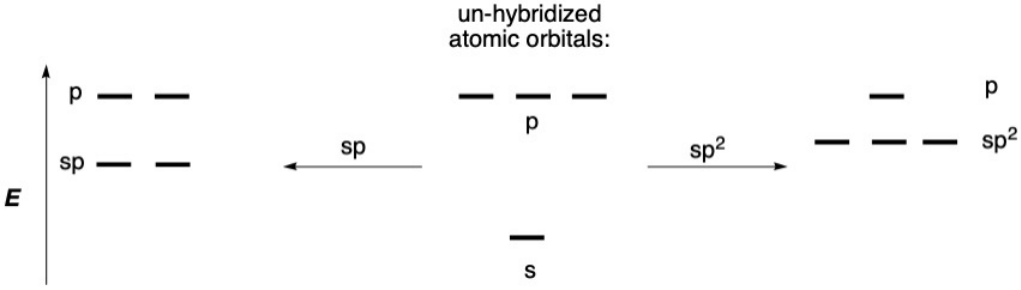
First, we need to draw the Lewis structures of each molecule, as shown below.



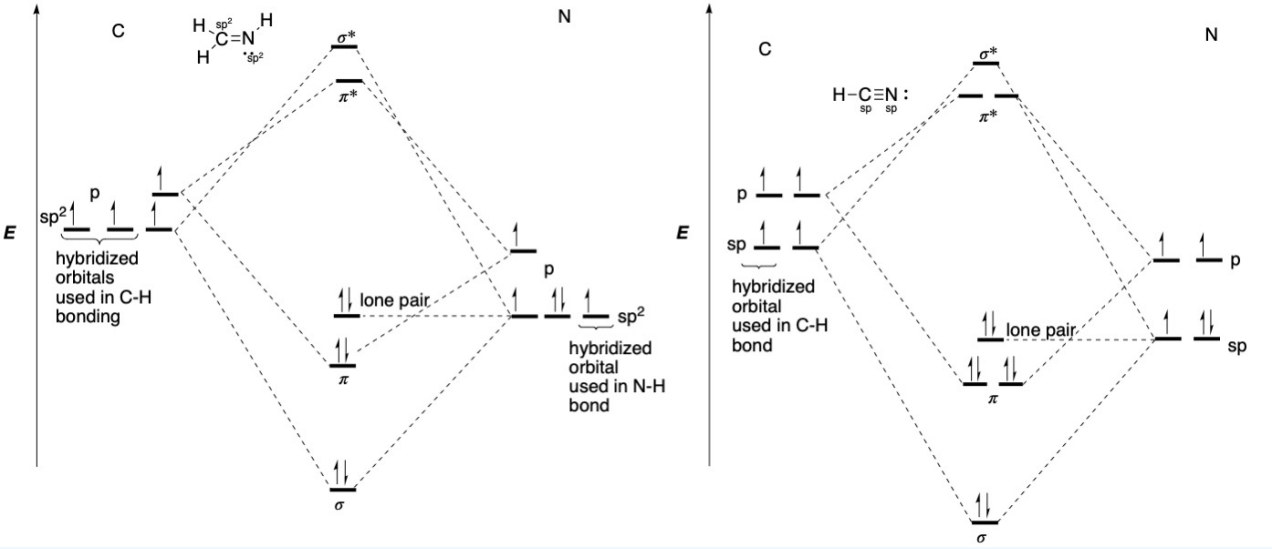
Then, we can assign their hybridizations based on the Lewis structures (Solution to A):



The hybridizations and Lewis structures will allow us to assign starting energies to the hybridized atomic orbitals:



Using these starting energies and the bonding shown in the Lewis structure, we can construct two hybridized orbital energy diagrams.



Now, using the hybridization of the N atoms in each diagram, we can see that an sp hybridized lone pair will be lower in energy than an sp^2 hybridized lone pair. Thus, the higher energy lone pair will be the lone pair in $H_2C{=}NH$.

Note 1: The nitrogen orbitals start lower in energy than the carbon orbitals, because N is more electronegative than C.

Note 2: The nitrogen orbitals are further apart than the carbon orbitals, because the s orbitals are more affected by electronegativity than p orbitals, which leads to a larger s/p orbital difference.

Drawing Bonding and Antibonding Orbitals Starting with Hybridized Orbitals

Figure 3.9.9 (above) shows a cartoon depiction of the bonding orbitals in ethene. These bonding orbitals are formed in the same way bonding orbitals in Molecular Orbital Diagrams are formed, through overlapping atomic orbitals. The corresponding antibonding orbitals can also be drawn in analogy to molecular orbitals (Chapter 3.2).

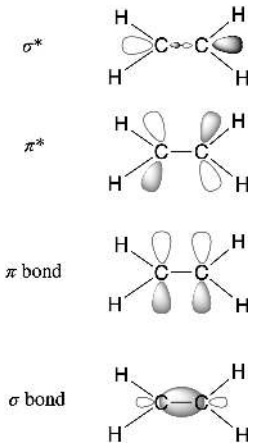


Figure 3.9.3 : bonding and antibonding orbitals formed with hybridized orbitals in ethene.

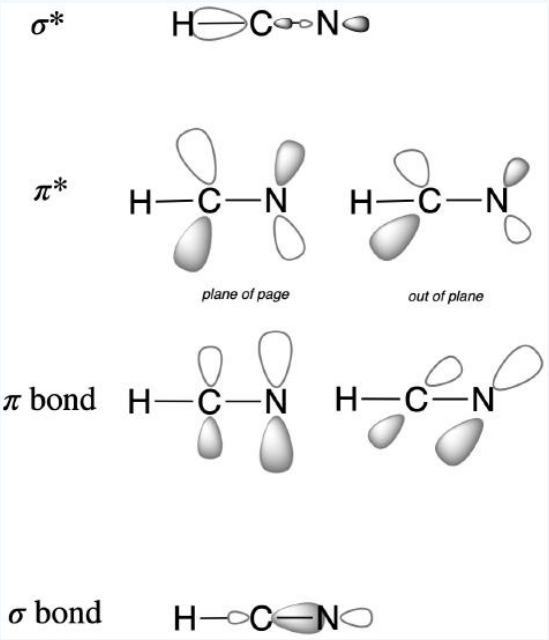
The orbitals shown in Figure 3.9.3 have left and right lobes with the same "orbital density" because the left and right atoms have identical atomic orbitals. These orbitals will distort based on the electronegativities and atomic orbital energies of the starting orbitals - so bonds with two different elements or different hybridizations will have different shapes.

✔ Example 3.9.3 : Drawing molecular orbitals with hybridized atoms with different electronegativities.

Draw the molecular orbitals (bonding and antibonding) corresponding to the C-N bond in HCN, using the solution to Exercise ✔ 3.9.2 .

Solution

The orbitals we need to draw are the σ, σ*, π, and π*. Looking at the solution to Exercise ✔ 3.9.2 , we can find ✔ that σ and π are closer in energy to N (more electronegative) and the σ* and π* are closer in energy to C. Thus, our bonding orbitals should be distorted toward N, and our antibonding orbitals will be distorted toward C.



Example 3.9.3 shows how the molecular orbitals formed from hybridized atomic orbitals appear when distorted by atoms with different electronegativities. The p orbitals are combined to form two perpendicular π orbitals (in plane and out of plane) and two perpendicular π* orbitals. The σ and σ* orbitals are formed through the combination of sp hybridized orbitals, and are distorted by the difference in electronegativity between carbon and nitrogen.

This page titled 3.9: Hybridized Orbital Energy Diagrams is shared under a not declared license and was authored, remixed, and/or curated by Alexandra Strom.

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

3.10: Key Terms

antibonding orbital
molecular orbital located outside of the region between two nuclei; electrons in an antibonding orbital destabilize the molecule

bond order
number of pairs of electrons between two atoms; it can be found by the number of bonds in a Lewis structure or by the difference between the number of bonding and antibonding electrons divided by two

bonding orbital
molecular orbital located between two nuclei; electrons in a bonding orbital stabilize a molecule

degenerate orbitals
orbitals that have the same energy

diamagnetism
phenomenon in which a material is not magnetic itself but is repelled by a magnetic field; it occurs when there are only paired electrons present

homonuclear diatomic molecule
molecule consisting of two identical atoms

hybrid orbital
orbital created by combining atomic orbitals on a central atom

hybridization
model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

linear combination of atomic orbitals
technique for combining atomic orbitals to create molecular orbitals

molecular orbital
region of space in which an electron has a high probability of being found in a molecule

molecular orbital diagram
visual representation of the relative energy levels of molecular orbitals

molecular orbital theory
model that describes the behavior of electrons delocalized throughout a molecule in terms of the combination of atomic wave functions

node
plane separating different lobes of orbitals, where the probability of finding an electron is zero

overlap
coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

paramagnetism
phenomenon in which a material is not magnetic itself but is attracted to a magnetic field; it occurs when there are unpaired electrons present

pi bond (π bond)
covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

s-p mixing
change that causes σ_p orbitals to be less stable than π_p orbitals due to the mixing of *s* and *p*-based molecular orbitals of similar energies.

sigma bond (σ bond)
covalent bond formed by overlap of atomic orbitals along the internuclear axis

***sp* hybrid orbital**
one of a set of two orbitals with a linear arrangement that results from combining one *s* and one *p* orbital

***sp*^{2} hybrid orbital**
one of a set of three orbitals with a trigonal planar arrangement that results from combining one *s* and two *p* orbitals

***sp*^{3} hybrid orbital**
one of a set of four orbitals with a tetrahedral arrangement that results from combining one *s* and three *p* orbitals

***sp*^{3}*d* hybrid orbital**
one of a set of five orbitals with a trigonal bipyramidal arrangement that results from combining one *s*, three *p*, and one *d* orbital

***sp*^{3}*d*^{2} hybrid orbital**
one of a set of six orbitals with an octahedral arrangement that results from combining one *s*, three *p*, and two *d* orbitals

valence bond theory
description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

π bonding orbital
molecular orbital formed by side-by-side overlap of atomic orbitals, in which the electron density is found on opposite sides of the internuclear axis

π* bonding orbital
antibonding molecular orbital formed by out of phase side-by-side overlap of atomic orbitals, in which the electron density is found on both sides of the internuclear axis, and there is a node between the nuclei

σ bonding orbital
molecular orbital in which the electron density is found along the axis of the bond

σ* bonding orbital
antibonding molecular orbital formed by out-of-phase overlap of atomic orbital along the axis of the bond, generating a node between the nuclei

---

This page titled 3.10: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

3.11: Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond. Dipole moments can be used to determine partial separations of charges between atoms.

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply *sp* hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (*p* or *d* orbitals).

Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from *s* orbitals or from *p* orbitals oriented in an end-to-end fashion. Molecular orbitals formed from *p* orbitals oriented in a side-by-side fashion have electron density on opposite sides of the internuclear axis and are called π orbitals.

We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

This page titled 3.11: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

3.12: Exercises

1.

Explain how σ and π bonds are similar and how they are different.

2.

Use valence bond theory to explain the bonding in F_2, HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.

3.

Use valence bond theory to explain the bonding in O_2. Sketch the overlap of the atomic orbitals involved in the bonds in O_2.

4.

How many σ and π bonds are present in the molecule HCN?

5.

A friend tells you N_2 has three π bonds due to overlap of the three *p*-orbitals on each N atom. Do you agree?

6.

Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.

(a) CO_2

(b) CO

7.

Why is the concept of hybridization required in valence bond theory?

8.

Give the shape that describes each hybrid orbital set:

(a) sp^2

(b) sp^3d

(c) sp

(d) sp^3d^2

9.

Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

10.

What is the hybridization of the central atom in each of the following?

(a) BeH_2

(b) SF_6

(c) $PO_4{}^{3-}$

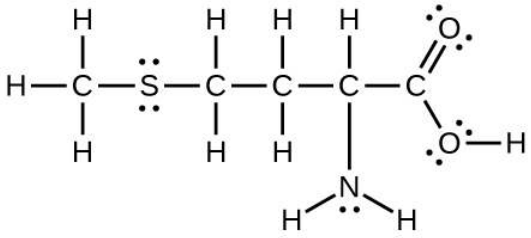
(d) PCl_5

11.

A molecule with the formula AB_3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

12.

Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. The Lewis structure of this compound is shown below. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?



13.

Sulfuric acid is manufactured by a series of reactions represented by the following equations:

$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

(a) circular S_8 molecule

(b) SO_2 molecule

(c) SO_3 molecule

(d) H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

14.

Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

$$2C_3H_8(g) \longrightarrow C_2H_4(g) + C_3H_6(g) + CH_4(g) + H_2(g)$$

For each of the four carbon compounds, do the following:

(a) Draw a Lewis structure.

(b) Predict the geometry about the carbon atom.

(c) Determine the hybridization of each type of carbon atom.

15.

Analysis of a compound indicates that it contains 77.55% Xe and 22.45% F by mass.

(a) What is the empirical formula for this compound? *(Assume this is also the molecular formula in responding to the remaining parts of this exercise).*

(b) Write a Lewis structure for the compound.

(c) Predict the shape of the molecules of the compound.

(d) What hybridization is consistent with the shape you predicted?

16.

Consider nitrous acid, HNO_2 (HONO).

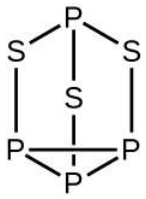
(a) Write a Lewis structure.

(b) What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the HNO_2 molecule?

(c) What is the hybridization on the internal oxygen and nitrogen atoms in HNO_2?

17.

Strike-anywhere matches contain a layer of $KClO_3$ and a layer of P_4S_3. The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match. $KClO_3$ contains the ClO_3^- ion. P_4S_3 is an unusual molecule with the skeletal structure.



(a) Write Lewis structures for P_4S_3 and the ClO_3^- ion.

(b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.

(c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.

(d) Determine the oxidation states and formal charge of the atoms in P_4S_3 and the ClO_3^- ion.

18.

Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)



19.

Write Lewis structures for NF_3 and PF_5. On the basis of hybrid orbitals, explain the fact that NF_3, PF_3, and PF_5 are stable molecules, but NF_5 does not exist.

20.

In addition to NF_3, two other fluoro derivatives of nitrogen are known: N_2F_4 and N_2F_2. What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

21.

The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a $C \equiv C$ triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

22.

For the carbonate ion, CO_3^{2-}, draw all of the resonance structures. Identify which orbitals overlap to create each bond.

23.

A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

(a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

(b) Identify the hybrid orbitals used by the carbon atoms in the molecule to form σ bonds.

(c) Describe the atomic orbitals that form the π bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

24.

For the molecule allene, $H_2C = C = CH_2$, give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

25.

Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

26.

Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

(a) H_3PO_4, phosphoric acid, used in cola soft drinks

(b) NH_4NO_3, ammonium nitrate, a fertilizer and explosive

(c) S_2Cl_2, disulfur dichloride, used in vulcanizing rubber

(d) $K_4[O_3POPO_3]$, potassium pyrophosphate, an ingredient in some toothpastes

27.

For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

(a) ozone (O_3) central O hybridization

(b) carbon dioxide (CO_2) central C hybridization

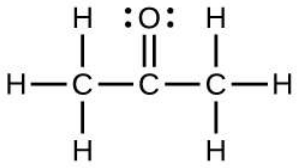
(c) nitrogen dioxide (NO_2) central N hybridization

(d) phosphate ion (PO_4^{3-}) central P hybridization

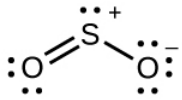
28.

For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

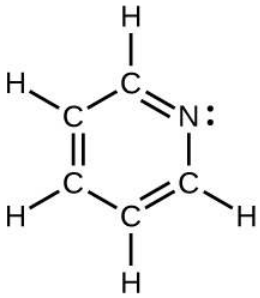
(a) Hybridization of each carbon



(b) Hybridization of sulfur



(c) All atoms



29.

Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.

30.

Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two *s* orbitals and from two *p* orbitals.

31.

How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) ψ for an atomic orbital and ψ for a molecular orbital

(c) bonding orbitals and antibonding orbitals

32.

If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

33.

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

34.

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

35.

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

36.

Calculate the bond order for an ion with this configuration:

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^3$$

37.

Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the 1*s* atomic orbital of either of the separated hydrogen atoms.

38.

Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

(a) Na_2^{2+}

(b) Mg_2^{2+}

(c) Al_2^{2+}

(d) Si_2^{2+}

(e) P_2^{2+}

(f) S_2^{2+}

(g) F_2^{2+}

(h) Ar_2^{2+}

39.

Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

(a) H_2, H_2^+, H_2^-

(b) O_2, O_2^{2+}, O_2^{2-}

(c) Li_2, Be_2^+, Be_2

(d) F_2, F_2^+, F_2^-

(e) N_2, N_2^+, N_2^-

40.

For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?

41.

Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

(a) H and H_2

(b) N and N_2

(c) O and O_2

(d) C and C_2

(e) B and B_2

42.

Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

43.

A friend tells you that the 2*s* orbital for fluorine starts off at a much lower energy than the 2*s* orbital for lithium, so the resulting σ_{2s} molecular orbital in F_2 is more stable than in Li_2. Do you agree?

44.

True or false: Boron contains $2s^2 2p^1$ valence electrons, so only one *p* orbital is needed to form molecular orbitals.

45.

What charge would be needed on F_2 to generate an ion with a bond order of 2?

46.

Predict whether the MO diagram for S_2 would show s-p mixing or not.

47.

Explain why N_2^{2+} is diamagnetic, while O_2^{4+}, which has the same number of valence electrons, is paramagnetic.

48.

Using the MO diagrams, predict the bond order for the stronger bond in each pair:

(a) B_2 or B_2^+

(b) F_2 or F_2^+

(c) O_2 or O_2^{2+}

(d) C_2^+ or C_2^-

This page titled 3.12: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

4: 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.

4.1: Introduction
4.2: Energy Basics
4.3: Calorimetry
4.4: Enthalpy
4.5: Strengths of Ionic and Covalent Bonds
4.6: Key Terms
4.7: Key Equations
4.8: Summary
4.9: Exercises

This page titled 4: Thermochemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

4.1: 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 4.1.1: 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.

The chemical bond is simply another form of energy, and its strength is indicated in exactly the same units as any other process involving energy. That is, in joules (or kilojoules) – or, when taken on a molar basis, in J/mol or kJ/mol. All of the principles involving energy we have examined up to now apply to bond energies exactly as they do to all other forms of energy: that is, energy may change form or be absorbed or released, but it cannot be created or destroyed. The energy of a chemical bond is indicated by the bond enthalpy, taken by convention to be the energy required to break a chemical bond. The same energy is released when a chemical bond is formed. Given that a chemical reaction involves breaking some bonds and making others, the enthalpy change for a chemical reaction can be estimated by analyzing the bonds broken and formed during the reaction. While this procedure gives an estimate of the overall enthalpy, it should be noted that a far more precise method involves using enthalpies of formation; the fact that there can be significant differences between, for example, an O–H bond in water and that in acetic acid accounts for the discrepancy in calculating ΔH using bond enthalpies versus the use of enthalpies of formation.

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 4.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

4.2: Energy Basics

Learning Objectives

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

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

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure 4.2.1). 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 4.2.1: 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 4.2.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a)



(b)

Figure 4.2.2: (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 4.2.3). 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.

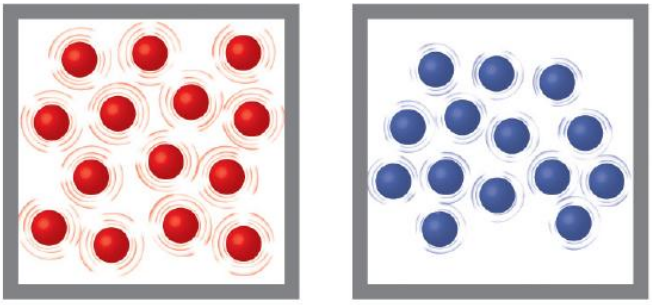


Figure 4.2.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

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 4.2.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

Figure 4.2.4: (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 4.2.5).

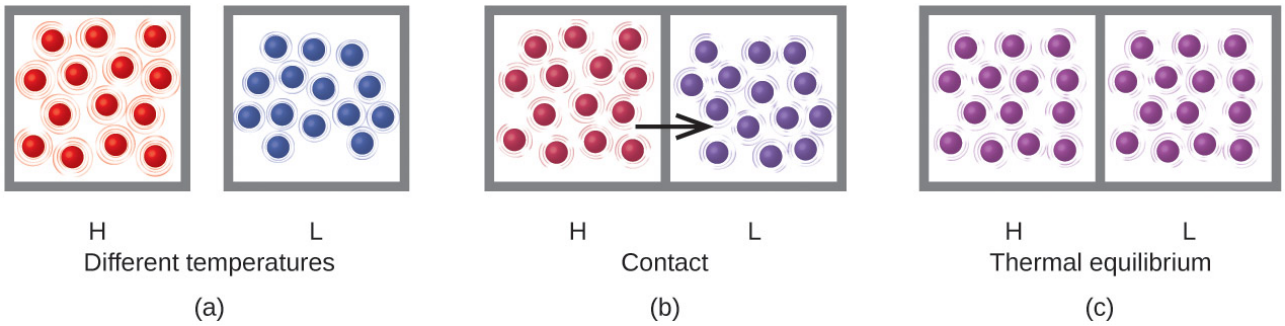


Figure 4.2.5: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two 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 4.2.6). 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 4.2.6: (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:

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

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:

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

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:

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

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:

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

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 4.2.7).

Figure 4.2.7: 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 4.2.1.

Table 4.2.1: 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:

$$\begin{aligned} q &= (\text{ specific heat }) \times (\text{ mass of substance }) \times (\text{ temperature change }) \\ &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned} \tag{4.2.1}$$

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 4.2.1: 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 4.2.1:

$$\begin{aligned} q &= c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= \left(4.184 J/\frac{g}{\circ}{}^{\circ}C\right) \times \left(8.0 \times 10^2 g\right) \times (85 - 21)^{\circ}C \\ &= (4.184 J/g^{\circ}C) \times \left(8.0 \times 10^2 g\right) \times (64)^{\circ}C \\ &= 210,000 J \left(= 2.1 \times 10^2 kJ\right) \end{aligned}$$

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

Exercise 4.2.1

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 4.2.2: 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 4.2.1:

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

Substituting the known values:

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

Solving:

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

Comparing this value with the values in Table 4.2.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 4.2.2

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

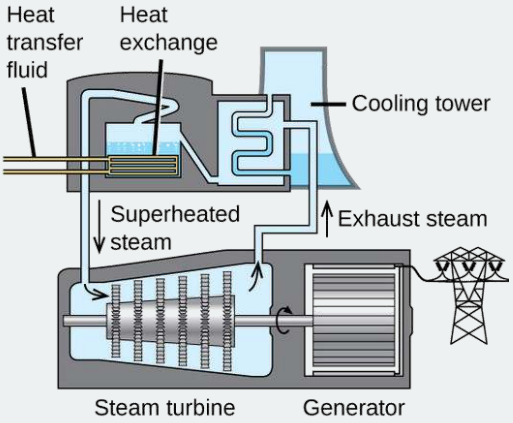
Chemistry in Everyday Life: Solar Thermal Energy Power Plants

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 4.2.8). 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 4.2.8: 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 4.2.9). 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.





Figure 4.2.9: (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 4.2: Energy Basics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

4.3: Calorimetry

Learning Objectives

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

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

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The 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 4.3.1). 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.

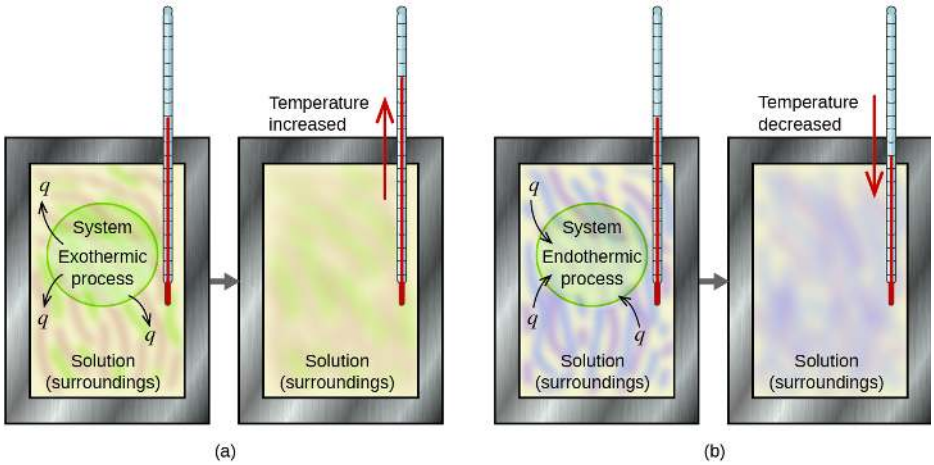


Figure 4.3.1: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred 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 4.3.2). These easy-to-use “coffee cup” calorimeters allow more heat exchange with the outside environment, and therefore produce less accurate energy values.

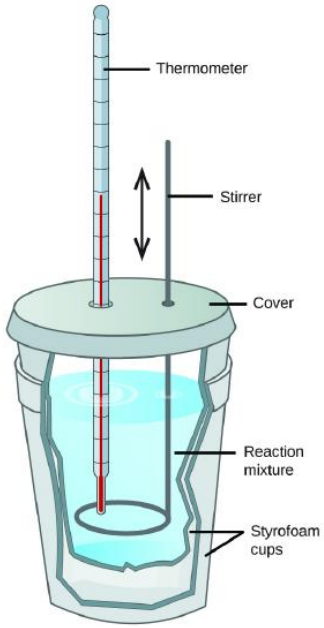


Figure 4.3.2: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

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 4.3.3).

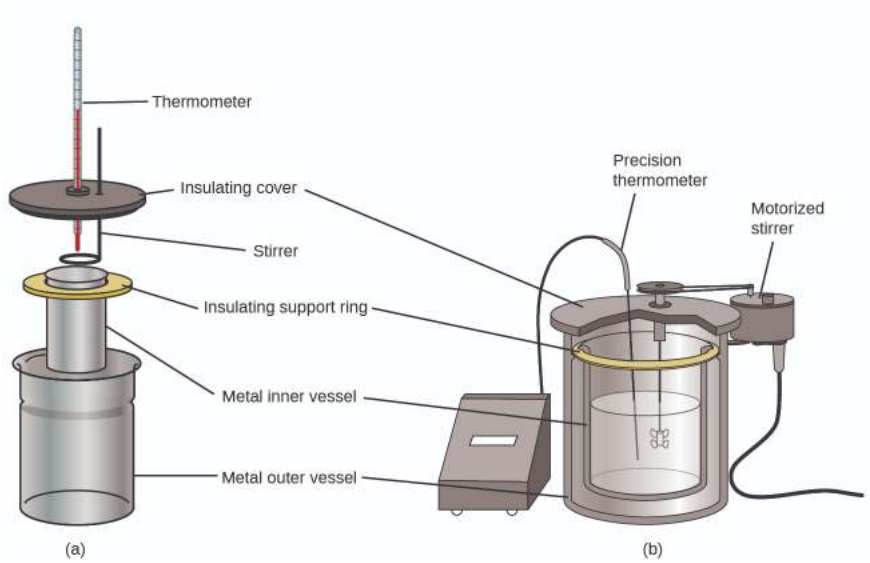


Figure 4.3.3: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

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 4.3.4). 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.

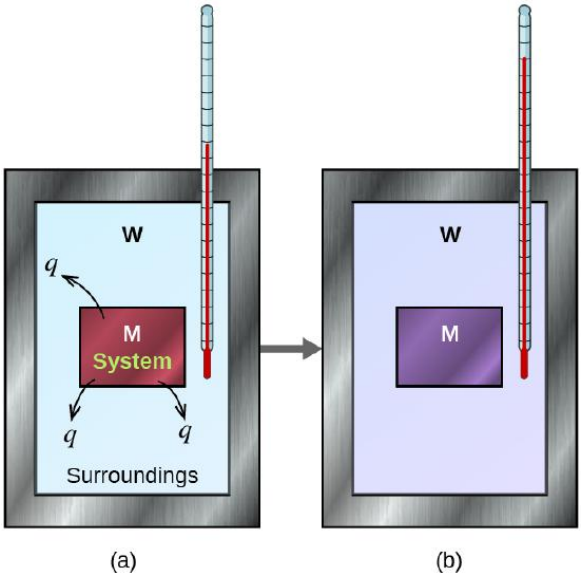


Figure 4.3.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 4.3.1: 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 4.3.1A

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 4.3.1B

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 4.3.2: 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:

$$(c_{\text{metal}})\,(59.7g)\,(28.5^{\circ}C - 100.0^{\circ}C) = -(4.18J/g^{\circ}C)\,(60.0g)\,(28.5^{\circ}C - 22.0^{\circ}C)$$

Solving this:

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

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 4.3.2

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 4.3.3: 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:

$$q_{solution} = \left(4.184 J/g^{\circ}C\right)\left(1.0 \times 10^2 g\right)\left(28.9^{\circ}C - 22.0^{\circ}C\right) = 2.9 \times 10^3 J$$

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 4.3.3

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 4.3.5). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process

$$NaC_2H_3O_2(aq) \longrightarrow NaC_2H_3O_2(s)$$

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 $NaC_2H_3O_2$ redissolves and can be reused.



Figure 4.3.5: 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

$$2\,Fe(s) + \tfrac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$$

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 4.3.4: 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 4.3.6). 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 4.3.6: 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 4.3.4

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 4.3.7). 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.

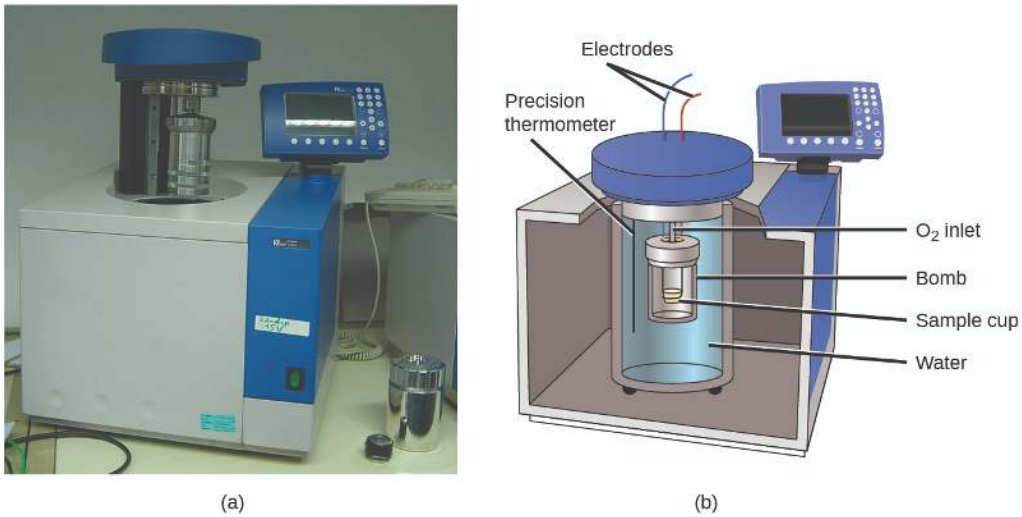


Figure 4.3.7: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work 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 4.3.5: 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 4.3.5

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 4.3.8).

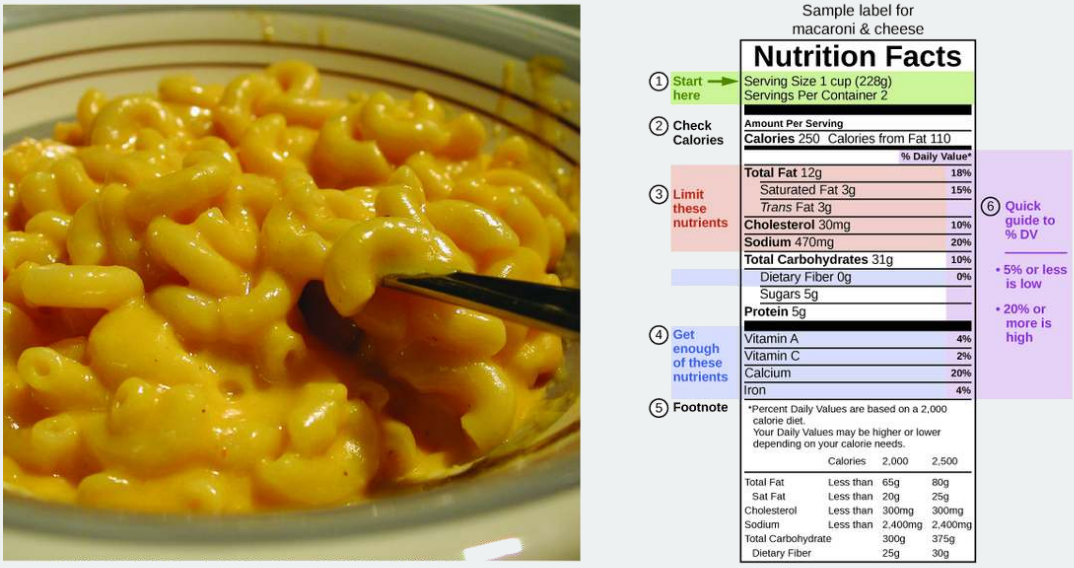


Figure 4.3.8: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification 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 4.3: Calorimetry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

4.4: Enthalpy

Learning Objectives

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

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

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

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

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

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

$$\Delta U = q + w$$

as shown in Figure 4.4.1. 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.

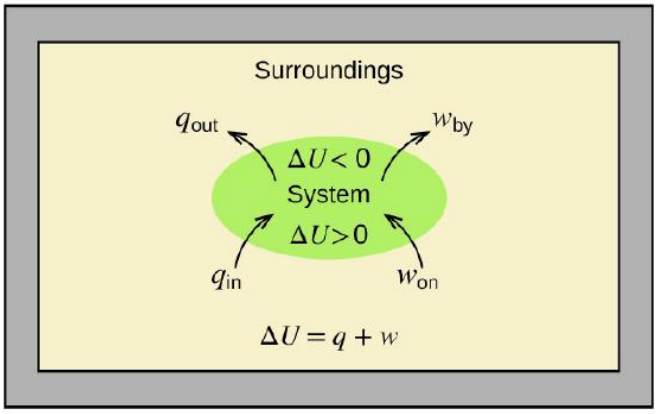


Figure 4.4.1: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal 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 4.4.2). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

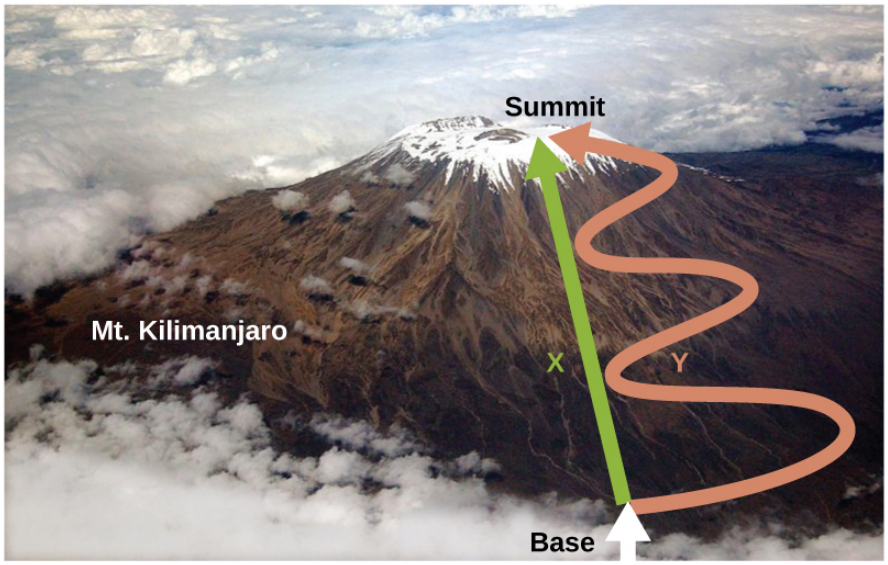


Figure 4.4.2: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; 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:

  $$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)} \quad \Delta H = -286 kJ$$

  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

    $$\mathrm{2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)} \quad \Delta H = 2 \times (-286 kJ) = -572 kJ$$

  - two-fold decrease in amounts

    $$\mathrm{\tfrac{1}{2}H_2(g) + \tfrac{1}{4}O_2(g) \longrightarrow \tfrac{1}{2}H_2O(l)} \quad \Delta H = \frac{1}{2} \times (-286 kJ) = -143 kJ$$

- 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.

  $$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)} \quad \Delta H = -242 kJ$$

Example 4.4.1: 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:

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

The thermochemical equation is then

$$\text{HCl(aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)} \quad \Delta H = -58kJ$$

? Exercise 4.4.1

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:

$$\text{Zn(s)} + 2\,\text{HCl(aq)} \longrightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$$

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction.

✓ Example 4.4.2: 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:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(aq)} + 8\,\text{KClO}_3\text{(aq)} \longrightarrow 12\,\text{CO}_2\text{(g)} + 11\,\text{H}_2\text{O(l)} + 8\,\text{KCl(aq)}$$

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

$$(2.67\,\text{g})\left(\frac{1\,\text{mol}}{342.3\,\text{g}}\right) = 0.00780\,\text{mol}\,\text{C}_{12}\text{H}_{22}\text{O}_{11}$$

$$(7.19\,\text{g})\left(\frac{1\,\text{mol}}{122.5\,\text{g}}\right) = 0.0587\,\text{mol}\,\text{KCIO}$$

The provided molar ratio of perchlorate-to-sucrose is then

$$\frac{0.0587\,\text{mol}\,\text{KClO}_3}{0.00780\,\text{mol}\,\text{C}_{12}\text{H}_{22}\text{O}_{11}} = 7.52$$

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:

$$\Delta H = \frac{-43.7\,\text{kJ}}{0.0587\,\text{molKClO}_3} = \frac{744\,\text{kJ}}{\text{mol}\,\text{KClO}_3}$$

Because the equation, as written, represents the reaction of 8 mol $KClO_3$, the enthalpy change is

$$\left(\frac{744\,\text{kJ}}{1\ \text{mol}\,\text{KClO}_3}\right)\left(8\ \text{mol}\,\text{KClO}_3\right) = 5960\,\text{kJ}$$

The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

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

Exercise 4.4.1

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

Answer

$\Delta H = -338$ 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.

$$\mathrm{C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2 + 3\,H_2O(l)} \quad \Delta H^\circ = -1366.8\,\mathrm{kJ}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 4.4.1. 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 4.4.1: 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

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH_c° (kJ/mol) at 25 °C
ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1366.8
methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$	−5461

Example 4.4.3: Using Enthalpy of Combustion

As Figure 4.4.3 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 4.4.3: 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 4.4.1 gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

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

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:

$$1.00\,\text{L}\,\text{C}_8\text{H}_{18} \longrightarrow 1.00 \times 10^3\ \text{mL}\,\text{C}_8\text{H}_{18}$$
$$1.00 \times 10^3\ \text{mL}\,\text{C}_8\text{H}_{18} \longrightarrow 692\,\text{g}\,\text{C}_8\text{H}_{18}$$
$$692\,\text{g}\,\text{C}_8\text{H}_{18} \longrightarrow 6.07\,\text{mol}\,\text{C}_8\text{H}_{18}$$
$$6.07\,\text{mol}\,\text{C}_8\text{H}_{18} \longrightarrow -3.31 \times 10^4 kJ$$

Exercise 4.4.3

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

Answer

6.25 10^3 kJ

https://chem.libretexts.org/@go/page/456052

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.



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 4.4.4).



Figure 4.4.4: 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:

$$\tfrac{1}{2}\mathrm{N_2(g)} + \mathrm{O_2(g)} \longrightarrow \mathrm{NO_2(g)} \quad \Delta H_f^\circ = \Delta H^\circ = +33.2\,\mathrm{kJ}$$

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 4.4.4: 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:

$$3\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{O_3(g)} \quad \Delta H^\circ = +286\,\mathrm{kJ}$$

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:

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

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 $\mathrm{O_3(g)}$:

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

Therefore,

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

Exercise 4.4.4

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

$$\mathrm{H_2(g)} + \mathrm{Cl_2(g)} \longrightarrow 2\,\mathrm{HCl(g)} \quad \Delta H^\circ = -184.6\,\mathrm{kJ}$$

Example 4.4.5: Writing Reaction Equations for

Write the heat of formation reaction equations for:

a. $\mathrm{C_2H_5OH(l)}$
b. $\mathrm{Ca_3(PO_4)_2(s)}$

Solution

Remembering that reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $$2\,\mathrm{C(s,\,graphite)} + 3\,\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{C_2H_5OH(l)}$$

b. $$3\,\mathrm{Ca(s)} + \tfrac{1}{2}\mathrm{P_4(s)} + 4\,\mathrm{O_2(g)} \longrightarrow \mathrm{Ca_3(PO_4)_2(s)}$$

Note: The standard state of carbon is graphite, and phosphorus exists as $\mathrm{P_4}$.

Exercise 4.4.5

Write the heat of formation reaction equations for:

a. $\mathrm{C_2H_5OC_2H_5(l)}$
b. $\mathrm{Na_2CO_3(s)}$

Answer

a. $$4\,\mathrm{C(s,\,graphite)} + 5\,\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{C_2H_5OC_2H_5(l)}$$

b. $$2\,\mathrm{Na(s)} + \mathrm{C(s,\,graphite)} + \tfrac{3}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{Na_2CO_3(s)}$$

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:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)} \quad \Delta H^\circ = -394kJ$$

In the two-step process, first carbon monoxide is formed:

$$\mathrm{C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)} \quad \Delta H^\circ = -111kJ$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\mathrm{CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)} \quad \Delta H^\circ = -283kJ$$

The equation describing the overall reaction is the sum of these two chemical changes:

step 1	$\mathrm{C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)}$
step 2	$\mathrm{CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)}$
sum	$\mathrm{C(s) + \cancel{CO(g)} + O_2(g) \longrightarrow \cancel{CO(g)} + CO_2(g)}$

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.

step 1	$\mathrm{C(s) + \frac{1}{2}O_2(g) \longrightarrow \cancel{CO(g)}}$	$\Delta H^\circ = -111\ \mathrm{kJ}$
step 2	$\mathrm{\cancel{CO(g)} + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)}$	$\Delta H^\circ = -283\ \mathrm{kJ}$
sum	$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)}$	$\Delta H^\circ = -394\ \mathrm{kJ}$

The result is shown in Figure 4.4.5. 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.

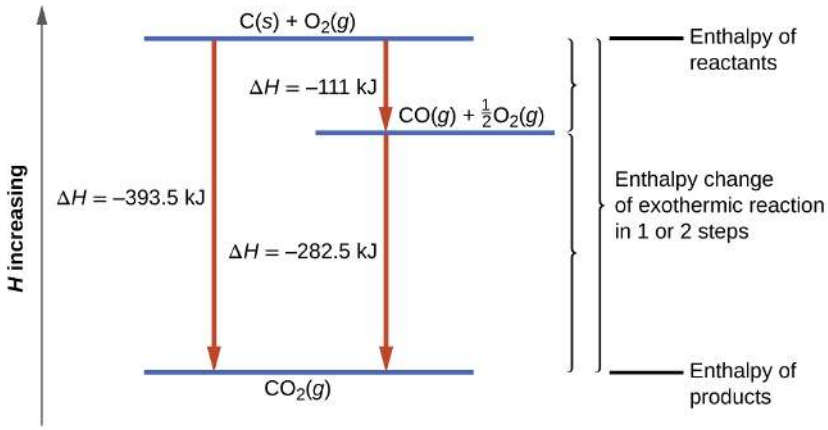


Figure 4.4.5: The formation of $\mathrm{CO_2(g)}$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

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:

$$\mathrm{\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)} \quad \Delta H = +33.2\ \mathrm{kJ}$$

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 ΔH 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 4.4.6: 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:

$$\mathrm{Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s)} \quad \Delta H^\circ = -341.8\ \mathrm{kJ}$$

$$\mathrm{FeCl_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow FeCl_3(s)} \quad \Delta H^\circ = -57.7\ \mathrm{kJ}$$

Solution

We are trying to find the standard enthalpy of formation of $\mathrm{FeCl_3(s)}$, which is equal to ΔH° for the reaction:

$$\mathrm{Fe(s) + \frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s)} \quad \Delta H_f^\circ = ?$$

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	$\mathrm{Fe(s) + Cl_2(g) \longrightarrow \cancel{FeCl_2(s)}}$	$\Delta H^\circ = -341.8\,\mathrm{kJ}$
step 2	$\mathrm{\cancel{FeCl_2(s)} + \frac{1}{2}Cl_2(g) \longrightarrow FeCl_3(s)}$	$\Delta H^\circ = -57.7\,\mathrm{kJ}$
sum	$\mathrm{Fe(s) + \frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s)}$	$\Delta H^\circ = -399.5\,\mathrm{kJ}$

The enthalpy of formation, ΔH_f° of $\mathrm{FeCl_3(s)}$ is −399.5 kJ/mol.

Exercise 4.4.6

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 4.4.7: 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 $\frac{1}{2}$:

$$\mathrm{ClF(g) + \tfrac{1}{2}O_2(g) \longrightarrow \tfrac{1}{2}Cl_2O(g) + \tfrac{1}{2}OF_2(g)} \quad \Delta H^\circ = \frac{1}{2}(214.0) = +107.0\,\mathrm{kJ}$$

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:

$$\mathrm{\tfrac{1}{2}O_2(g) + F_2(g) \longrightarrow OF_2(g)} \quad \Delta H^\circ = +24.7\,\mathrm{kJ}$$

To get $\mathrm{ClF_3}$ as a product, reverse (iv), changing the sign of ΔH^o:

$$\mathrm{\tfrac{1}{2}Cl_2O(g) + \tfrac{3}{2}OF_2(g) \longrightarrow ClF_3(g) + O_2(g)} \quad \Delta H^\circ = -236.2kJ$$

Now check to make sure that these reactions add up to the reaction we want:

step 1	$\mathrm{ClF(g)} + \cancel{\frac{1}{2}\mathrm{O_2(g)}} \longrightarrow \cancel{\frac{1}{2}\mathrm{Cl_2O(g)}} + \cancel{\frac{1}{2}\mathrm{OF_2(g)}}$	$\Delta H^\circ = +107.0\,\mathrm{kJ}$
step 2	$\cancel{\frac{1}{2}\mathrm{O_2(g)}} + \mathrm{F_2(g)} \longrightarrow \cancel{\mathrm{OF_2(g)}}$	$\Delta H^\circ = +24.7\,\mathrm{kJ}$
step 3	$\cancel{\frac{1}{2}\mathrm{Cl_2O(g)}} + \cancel{\frac{3}{2}\mathrm{OF_2(g)}} \longrightarrow \mathrm{ClF_3(g)} + \cancel{\mathrm{O_2(g)}}$	$\Delta H^\circ = -236.2\,\mathrm{kJ}$
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 4.4.7

Aluminum chloride can be formed from its elements:

i. $$2\,\mathrm{Al(s)} + 3\,\mathrm{Cl_2(g)} \longrightarrow 2\,\mathrm{AlCl_3(s)} \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction *(i)*:

ii. $$\mathrm{HCl(g)} \longrightarrow \mathrm{HCl(aq)} \quad \Delta H^\circ_{(ii)} = -74.8\,\mathrm{kJ}$$

iii. $$\mathrm{H_2(g)} + \mathrm{Cl_2(g)} \longrightarrow 2\,\mathrm{HCl(g)} \quad \Delta H^\circ_{(iii)} = -185\,\mathrm{kJ}$$

iv. $$\mathrm{AlCl_3(aq)} \longrightarrow \mathrm{AlCl_3(s)} \quad \Delta H^\circ_{(iv)} = +323\,\mathrm{kJ}$$

v. $$2\,\mathrm{Al(s)} + 6\,\mathrm{HCl(aq)} \longrightarrow 2\,\mathrm{AlCl_3(aq)} + 3\,\mathrm{H_2(g)} \quad \Delta H^\circ_{(v)} = -1049\,\mathrm{kJ}$$

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 $\sum$ 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 4.4.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,\mathrm{NO_2(g)} + \mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{HNO_3(aq)} + \mathrm{NO(g)} \quad \Delta H^\circ = ?$$

Solution: Using the Equation

Use the special form of Hess's law given previously, and values from Appendix G:

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants }) \\ &= \left[2\ \text{mol}\,\cancel{\text{HNO}_3\text{(aq)}} \times \frac{-207.4\,\text{kJ}}{1\ \text{mol}\,\cancel{\text{HNO}_3\text{(aq)}}} + 1\ \text{mol}\,\cancel{\text{NO(g)}} \times \frac{+90.2\,\text{kJ}}{1\ \text{mol}\,\cancel{\text{NO(g)}}}\right] \\ &\quad - \left[3\ \text{mol}\,\cancel{\text{NO}_2\text{(g)}} \times \frac{+33.2\,\text{kJ}}{1\ \text{mole}\,\cancel{\text{NO}_2\text{(g)}}} + 1\ \text{mol}\,\cancel{\text{H}_2\text{O(l)}} \times \frac{-285.8\,\text{kJ}}{1\ \text{mol}\,\cancel{\text{H}_2\text{O(l)}}}\right] \\ &= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)] \\ &= -323.03 + 186.23 \\ &= -136.80\,\text{kJ}\end{aligned}$$

Solution: Supporting Why the General Equation is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\,\text{NO}_2\text{(g)}$ and $H2O(l)$ into their constituent elements, and the formation of $2\,\text{HNO}_3\text{(aq)}$ and $1\,\text{NO(g)}$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH° values for these compounds (from Appendix G), we have:

$$\begin{aligned} 3\,\text{NO}_2\text{(g)} &\longrightarrow \tfrac{3}{2}\text{N}_2\text{(g)} + 3\,\text{O}_2\text{(g)} && \Delta H^\circ_1 = -99.6\,\text{kJ} \\ \text{H}_2\text{O(l)} &\longrightarrow \text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} && \Delta H^\circ_2 = +285.8\,\text{kJ}\left[-1 \times \Delta H^\circ_f(\text{H}_2\text{O})\right] \\ \text{H}_2\text{(g)} + \text{N}_2\text{(g)} + 3\,\text{O}_2\text{(g)} &\longrightarrow 2\,\text{HNO}_3\text{(aq)} && \Delta H^\circ_3 = -414.8\,\text{kJ}\left[2 \times \Delta H^\circ_f(\text{HNO}_3)\right] \\ \tfrac{1}{2}\text{N}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} &\longrightarrow \text{NO(g)} && \Delta H^\circ_4 = +90.2\,\text{kJ}\left[1 \times \Delta H^\circ_f(\text{NO})\right] \end{aligned}$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,\text{NO}_2\text{(g)} + \text{H}_2\text{O(l)} \longrightarrow 2\,\text{HNO}_3\text{(aq)} + \text{NO(g)}$$

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 4.4.8

Calculate the heat of combustion of 1 mole of ethanol, $\text{C}_2\text{H}_5\text{OH(l)}$, when $\text{H}_2\text{O(l)}$ and $\text{CO}_2\text{(g)}$ are formed. Use the following enthalpies of formation: $\text{C}_2\text{H}_5\text{OH(l)}$, −278 kJ/mol; $\text{H}_2\text{O(l)}$, −286 kJ/mol; and $\text{CO}_2\text{(g)}$, −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 4.4: Enthalpy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

4.5: Strengths of Ionic and Covalent Bonds

Learning Objectives

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

- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of reaction

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy. The stronger a bond, the greater the energy required to break it.

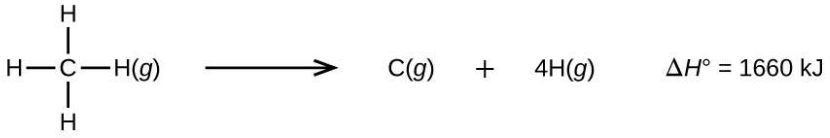
The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, $D_{X–Y}$, is defined as the **standard enthalpy change** for the endothermic reaction:

$$XY(g) \longrightarrow X(g) + Y(g) \quad D_{X–Y} = \Delta H^\circ$$

For example, the bond energy of the pure covalent H–H bond, $D_{H–H}$, is 436 kJ per mole of H–H bonds broken:

$$H_2(g) \longrightarrow 2H(g) \quad D_{H–H} = \Delta H^\circ = 436\ \text{kJ}$$

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH_4, 1660 kJ, is equal to the standard enthalpy change of the reaction:



The average C–H bond energy, $D_{C–H}$, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 4.5.1, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 4.5.2. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table 4.5.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395		418	Si–Cl	359
H–P	320		946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
	611	O–O	140	P–I	215
	837		498	S–S	215
C–N	290	O–F	160	S–Cl	250
	615	O–Si	370	S–Br	215
	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
	741	O–I	200	Cl–I	210
	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 4.5.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
	1.34	611
	1.20	837
C–N	1.43	290
	1.38	615
	1.16	891
C–O	1.43	350
	1.23	741
	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic. An exothermic reaction (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, ΔH, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy "in", positive sign) plus the energy released when all bonds are formed in the products (energy "out," negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$

In this expression, the symbol Σ means "the sum of" and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table (like Table 4.5.2) and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

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

or

$$\mathrm{H{-}H(g) + Cl{-}Cl(g) \longrightarrow 2\,H{-}Cl(g)}$$

To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2 432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned}\Delta H &= \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \\ &= [D_{H-H} + D_{Cl-Cl}] - [2\,(D_{H-Cl})] \qquad = [436 + 243] - 2(432) = -185kJ\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Appendix G gives a value for the standard molar enthalpy of formation of HCl(g), ΔH_f^o of –92.307 kJ/mol. Twice that value is –184.6 kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

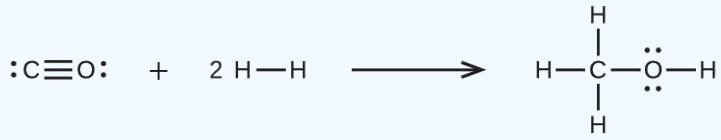
Example 4.5.1: Using Bond Energies to Calculate Approximate Enthalpy Changes

Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table 4.5.2, calculate the approximate enthalpy change, ΔH, for the reaction here:

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

Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\begin{aligned}\Delta H &= \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \\ &= [D_{C\equiv O} + 2\,(D_{H-H})] - [3\,(D_{C-H}) + D_{C-O} + D_{O-H}]\end{aligned}$$

Using the bond energy values in Table 4.5.2, we obtain:

$$\begin{aligned}\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107kJ\end{aligned}$$

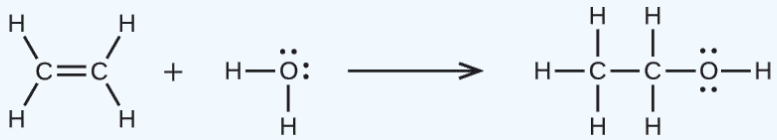
We can compare this value to the value calculated based on data from Appendix G:

$$\begin{aligned}\Delta H &= \left[\Delta H_f^\circ CH_3OH(g)\right] - \left[\Delta H_f^\circ CO(g) + 2 \times \Delta H_f^\circ H_2\right] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5kJ\end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

? Exercise 4.5.1

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



Using the bond energies in Table 4.5.2, calculate an approximate enthalpy change, Δ*H*, for this reaction.

Answer

–35 kJ

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy** ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX(s) \longrightarrow M^{n+}(g) + X^{n-}(g) \quad \Delta H_{\text{lattice}}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{\text{lattice}}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{C\,(Z^+)\,(Z^-)}{R_0}$$

in which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and R_o is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 4.5.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

Exercise 4.5.1

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Answer

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The **Born-Haber cycle** is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f° the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s° the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal
- $\Delta H_{lattice}$, the lattice energy of the compound

Figure 4.5.1: diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

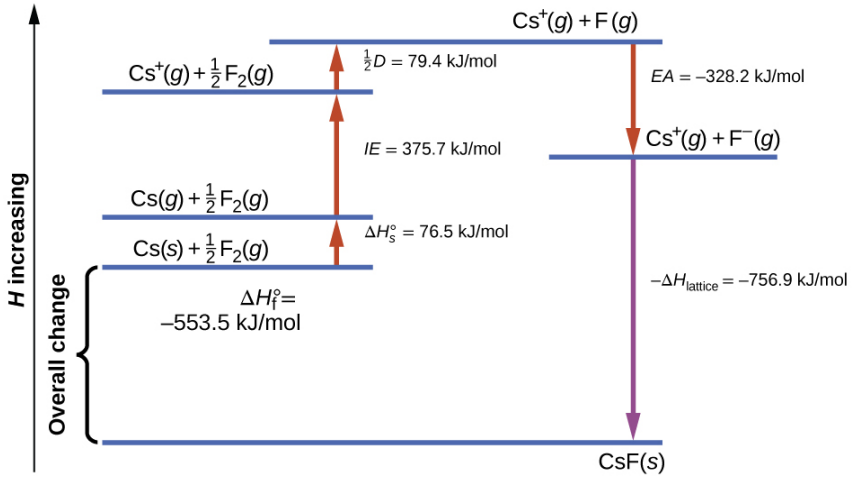


Figure 4.5.1: The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

We begin with the elements in their most common states, $\mathrm{Cs(s)}$ and $\mathrm{F_2(g)}$. The represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the *y*-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is

equal to the experimentally determined enthalpy of formation, ΔH_f° of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 4.5.3 shows this for fluoride, CsF.

Table 4.5.3

Enthalpy of sublimation of Cs(s)	$\mathrm{Cs(s)} \longrightarrow \mathrm{Cs(g)}$	$\Delta H = \Delta H_s^\circ = 76.5\,\mathrm{kJ/mol}$
One-half of the bond energy of $\mathrm{F_2}$	$\frac{1}{2}\mathrm{F_2(g)} \longrightarrow \mathrm{F(g)}$	$\Delta H = \frac{1}{2}D = 79.4\,\mathrm{kJ/mol}$
Ionization energy of Cs(g)	$\mathrm{Cs(g)} \longrightarrow \mathrm{Cs^+(g) + e^-}$	$\Delta H = IE = 375.7\,\mathrm{kJ/mol}$
Electron affinity of F	$\mathrm{F(g) + e^-} \longrightarrow \mathrm{F^-(g)}$	$\Delta H = EA = -328.2\,\mathrm{kJ/mol}$
Negative of the lattice energy of CsF(s)	$\mathrm{Cs^+(g) + F^-(g)} \longrightarrow \mathrm{CsF(s)}$	$\Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of CsF(s), add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (EA) + (-\Delta H_{\text{lattice}})$ $\mathrm{Cs(s)} + \frac{1}{2}\mathrm{F_2(g)} \longrightarrow \mathrm{CsF(s)}$	$\Delta H = -553.5\,\mathrm{kJ/mol}$

Thus, the lattice energy can be calculated from other values. For cesium fluoride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = 76.5 + 79.4 + 375.7 + (-328.2) - (-553.5) = 756.9\,\mathrm{kJ/mol}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_s°, ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_{\text{lattice}}$, and standard enthalpy of formation are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much higher than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

This page titled 4.5: Strengths of Ionic and Covalent Bonds is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

- **7.5: Strengths of Ionic and Covalent Bonds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.6: 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

bond energy
(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Born-Haber cycle
thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

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 $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

lattice energy ($\Delta H_{\text{lattice}}$)

energy required to separate one mole of an ionic solid into its component gaseous ions

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 (ΔH_c°)

heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH_f°)

enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard 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

---

This page titled 4.6: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

4.7: Key Equations

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

$\Delta U = q +$
$\Delta H_{\text{reaction}}{}^{\circ} = \sum n \times \Delta H_{\text{f}}{}^{\circ}(\text{products}) - \sum n \times \Delta H_{\text{f}}{}^{\circ}(\text{reactants})$

Bond energy for a diatomic molecule: $\text{XY}(g) \longrightarrow \text{X}(g) + \text{Y}(g)$	$\text{D}_{\text{X–Y}} = \Delta H^{\circ}$
Enthalpy change: $\Delta H = \Sigma \text{D}_{\text{bonds broken}} - \Sigma \text{D}_{\text{bonds formed}}$	

This page titled 4.7: Key Equations is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

4.8: 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 ΔH° for reactions occurring under standard state conditions at 298 K. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. The standard enthalpy of formation, ΔH_f°, 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.

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

This page titled 4.8: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

4.9: 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 9.1, 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 9.1, 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 9.5 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 9.6 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 9.6 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 9.12. 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 9.12, 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 9.12). 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 9.12) 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 9.5 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 9.6 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 9.17), 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 9.5 differs from the enthalpy change for the exothermic reaction described by the following equation:
$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$

40.

Using the data in the check your learning section of Example 9.5, calculate ΔH in kJ/mol of $\mathrm{AgNO_3}(aq)$ for the reaction: $\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq)$

41.

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $\mathrm{NH_4NO_3}$ under the conditions described in Example 9.6.

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.)
$\mathrm{Ba(OH)_2 \cdot 8H_2O}(s) + 2\mathrm{NH_4SCN}(aq) \longrightarrow \mathrm{Ba(SCN)_2}(aq) + 2\mathrm{NH_3}(aq) + 10\mathrm{H_2O}\,(l)$

43.

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $\mathrm{CaCl_2}$ (refer to Exercise 9.25).

44.

Although the gas used in an oxyacetylene torch (Figure 9.7) 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 9.2. 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?

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

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 $\mathrm{SO_2}(l) \longrightarrow \mathrm{SO_2}(g)$ and $\mathrm{CCl_2F}\,(l) \longrightarrow \mathrm{CCl_2F_2}(g)$, 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 9.2 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 $\mathrm{2H_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2H_2O}\,(g)$?

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:

$\mathrm{4NH_3}(g) + \mathrm{5O_2}(g) \longrightarrow \mathrm{4NO}\,(g) + \mathrm{6H_2O}\,(l) \qquad \Delta H = -907\ \mathrm{kJ}$

$\mathrm{2NO}\,(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2NO_2}(g) \qquad \Delta H = -113\ \mathrm{kJ}$

$\mathrm{3NO_2} + \mathrm{H_2O}\,(l) \longrightarrow \mathrm{2HNO_3}(aq) + \mathrm{NO}(g) \qquad \Delta H = -139\ \mathrm{kJ}$

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

60.

Both graphite and diamond burn.
$\mathrm{C}\,(s,\ \text{diamond}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$

For the conversion of graphite to diamond:
$\mathrm{C}\,(s,\ \text{graphite}) \longrightarrow \mathrm{C}\,(s,\ \text{diamond}) \qquad \Delta H^\circ = 1.90\ \text{kJ}$

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:
$\mathrm{H_2O}\,(l) \longrightarrow \mathrm{H_2O}\,(g)$

62.

Which produces more heat?
$\mathrm{Os}\,(s) \longrightarrow 2\mathrm{O_2}(g) \longrightarrow \mathrm{OsO_4}(s)$
or
$\mathrm{Os}\,(s) \longrightarrow 2\mathrm{O_2}(g) \longrightarrow \mathrm{OsO_4}(g)$
for the phase change $\mathrm{OsO_4}(s) \longrightarrow \mathrm{OsO_4}(g) \qquad \Delta H = 56.4\ \text{kJ}$

63.

Calculate ΔH° for the process
$\mathrm{Sb}\,(s) + \frac{5}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_5}(s)$
from the following information:

$\mathrm{Sb}\,(s) + \frac{3}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_3}(s) \qquad \Delta H^\circ = -314\ \text{kJ}$
$\mathrm{SbCl_3}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_5}(s) \qquad \Delta H^\circ = -80\ \text{kJ}$

64.

Calculate ΔH° for the process $\mathrm{Zn}\,(s) + \mathrm{S}\,(s) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{ZnSO_4}(s)$
from the following information:
$\mathrm{Zn}(s) + \mathrm{S}(s) \longrightarrow \mathrm{ZnS}(s) \qquad \Delta H^\circ = -206.0\ \text{kJ}$
$\mathrm{ZnS}(s) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{ZnSO_4}(s) \qquad \Delta H^\circ = -776.8\ \text{kJ}$

65.

Calculate ΔH for the process $\mathrm{Hg_2Cl_2}(s) \longrightarrow 2\mathrm{Hg}\,(l) + \mathrm{Cl_2}(g)$
from the following information:
$\mathrm{Hg}(l) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{HgCl_2}(s) \qquad \Delta H = -224\ \text{kJ}$
$\mathrm{Hg}(l) + \mathrm{HgCl_2}(s) \longrightarrow \mathrm{Hg_2Cl_2}(s) \qquad \Delta H = -41.2\ \text{kJ}$

66.

Calculate ΔH° for the process $\mathrm{Co_3O_4}(s) \longrightarrow 3\mathrm{Co}\,(s) + 2\mathrm{O_2}(g)$
from the following information:

$\mathrm{Co}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CoO}(s) \qquad \Delta H^\circ = -237.9\text{kJ}$
$3\mathrm{CoO}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Co_3O_4}(s) \qquad \Delta H^\circ = -177.5\text{kJ}$

67.

Calculate the standard molar enthalpy of formation of NO(g) from the following data:

$N_2(g) + 2O_2 \longrightarrow 2NO_2(g) \qquad \Delta H^\circ = 66.4\ \text{kJ}$

$2NO(g) + O_2 \longrightarrow 2NO_2(g) \qquad \Delta H^\circ = -114.1\ \text{kJ}$

68.

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

(b) $Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(g)$

(c) $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

69.

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) $Si(s) + 2F_2(g) \longrightarrow SiF_4(g)$

(b) $2C(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3CO_2H(l)$

(c) $CH_4(g) + N_2(g) \longrightarrow HCN(g) + NH_3(g)$;

(d) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

70.

The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.

(a) $2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$

(b) $SnO(s) + CO(g) \longrightarrow Sn(s) + CO_2(g)$

(c) $Cr_2O_3(s) + 3H_2(g) \longrightarrow 2Cr(s) + 3H_2O(l)$

(d) $2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$

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.

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

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: $\mathrm{TiCl_4}(g) + 2\mathrm{H_2O}(g) \longrightarrow \mathrm{TiO_2}(s) + 4\mathrm{HCl}(g)$.

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: $\mathrm{C}(s) + \mathrm{H_2O}(g) \longrightarrow \mathrm{CO}(g) + \mathrm{H_2}(g)$.

(a) Assuming that coke has the same enthalpy of formation as graphite, calculate ΔH° for this reaction.

(b) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst: $2\mathrm{H_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{CH_3OH}(g)$.

Under the conditions of the reaction, methanol forms as a gas. Calculate ΔH° 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:
$\mathrm{CaC_2}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s) + \mathrm{C_2H_2}(g)$.
Calculate the standard enthalpy of the reaction. The ΔH_f° of CaC_2 is −15.14 kcal/mol.

78.

From the data in Table 9.2, 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} ($\Delta H_f^\circ = -208.4\ \mathrm{kJ/mol}$; 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 Unexpected text node: 'Appendix G.'

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. $\mathrm{C_2H_4}(g) + \mathrm{H_2O}(g) \longrightarrow \mathrm{C_2H_5OH}(l)$

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:
$\mathrm{C_6H_{12}O_6}(s) + 6\mathrm{O_2}(g) \longrightarrow 6\mathrm{CO_2}(g) + 6\mathrm{H_2O}(l) \qquad \Delta H = -2816\ \mathrm{kJ}$

The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.

(a) How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?

(b) How many Calories can be produced by the metabolism of 1.0 g of glucose?

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, ΔH_f° of propane given that ΔH_f° of $H_2O(l)$ = −285.8 kJ/mol and ΔH_f° of $CO_2(g)$ = −393.5 kJ/mol.

(d) Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

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) Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.

(b) How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8: density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $CO_2(g)$ and $H_2O(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.

(c) What mass of carbon dioxide is produced by combustion of the methane used to heat the house?

(d) What mass of water is produced by combustion of the methane used to heat the house?

(e) What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.

(f) How many kilowatt–hours (1 kWh = 3.6×10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.

(g) Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain

type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

87.

Which bond in each of the following pairs of bonds is the strongest?

(a) C–C or $\mathrm{C=C}$

(b) C–N or $\mathrm{C\equiv N}$

(c)$\mathrm{C\equiv O}$ or $\mathrm{C=O}$

(d) H–F or H–Cl

(e) C–H or O–H

(f) C–N or C–O

88.

Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $\mathrm{H_2}(g) + \mathrm{Br_2}(g) \longrightarrow 2\mathrm{HBr}\,(g)$

(b) $\mathrm{CH_4}(g) + \mathrm{I_2}(g) \longrightarrow \mathrm{CH_3I}\,(g) + \mathrm{HI}\,(g)$

(c) $\mathrm{C_2H_4}(g) + 3\mathrm{O_2}(g) \longrightarrow 2\mathrm{CO_2}(g) + 2\mathrm{H_2O}\,(g)$

89.

Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $\mathrm{Cl_2}(g) + 3\mathrm{F_2}(g) \longrightarrow 2\mathrm{ClF_3}(g)$

(b) $\mathrm{H_2C=CH_2}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{H_3CCH_3}(g)$

(c) $2\mathrm{C_2H_6}(g) + 7\mathrm{O_2}(g) \longrightarrow 4\mathrm{CO_2}(g) + 6\mathrm{H_2O}\,(g)$

90.

Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.

(a) Use the bond energy found in Table 9.3 and Table 9.4 to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)

(b) Use the enthalpy of reaction and the bond energies for $\mathrm{H_2}$ and $\mathrm{Cl_2}$ to solve for the energy of one mole of HCl bonds.

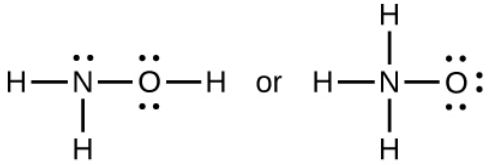
$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\mathrm{HCl}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -184.7\ \mathrm{kJ/mol}$$

91.

Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

92.

When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



93.

How does the bond energy of HCl(g) differ from the standard enthalpy of formation of HCl(g)?

94.

Using the standard enthalpy of formation data in Appendix G, show how the standard enthalpy of formation of HCl(g) can be used to determine the bond energy.

95.

Using the standard enthalpy of formation data in Appendix G, calculate the bond energy of the carbon-sulfur double bond in CS_2.

96.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

97.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

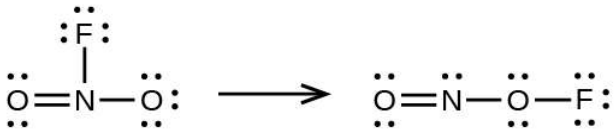
98.

Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:



99.

Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of FNO_2?



100.

Use principles of atomic structure to answer each of the following:[4]

(a) The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.

(b) The lattice energy of CaO(s) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.

(c) Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

(d) The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

101.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

102.

For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

(a) MgO

(b) SrO

(c) KF

(d) CsF

(e) MgF_2

103.

The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $M(s) + X_2(g) \longrightarrow MX_2(s)$. For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.

(a) a large radius vs. a small radius for M^{+2}

(b) a high ionization energy vs. a low ionization energy for M

(c) an increasing bond energy for the halogen

(d) a decreasing electron affinity for the halogen

(e) an increasing size of the anion formed by the halogen

104.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

105.

Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^+ have similar radii; O^{2-} and F^- have similar radii. Explain your choices.

(a) MgO or MgSe

(b) LiF or MgO

(c) Li_2O or LiCl

(d) Li_2Se or MgO

106.

Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and

K^+ have similar radii; S^{2-} and Cl^- have similar radii. Explain your choices.

(a) K_2O or Na_2O

(b) K_2S or BaS

(c) KCl or BaS

(d) BaS or $BaCl_2$

107.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) MgO

(b) SrO

(c) KF

(d) CsF

(e) MgF_2

108.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) K_2S

(b) K_2O

(c) CaS

(d) Cs_2S

(e) CaO

109.

The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F

distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol, 924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

Footnotes

- 4This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

This page titled 4.9: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

5: 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.

5.1: Introduction
5.2: Spontaneity
5.3: Entropy
5.4: The Second and Third Laws of Thermodynamics
5.5: Free Energy
5.6: Key Terms
5.7: Key Equations
5.8: Summary
5.9: Exercises

This page titled 5: Thermodynamics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

5.1: 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 5.1.1: 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)

This page titled 5.1: Introduction is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

- **16.0: Introduction** is licensed CC BY 4.0.

5.2: 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 5.2.1).

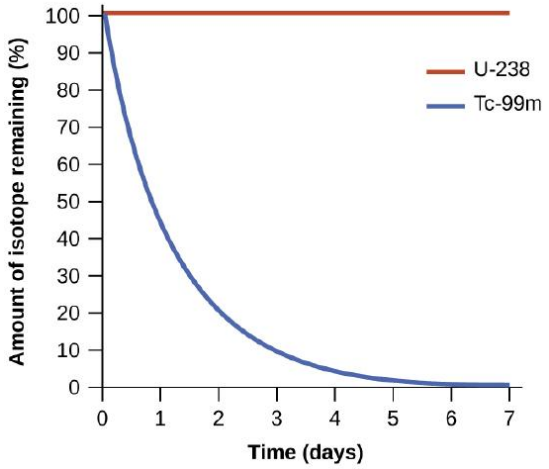


Figure 5.2.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure 5.2.2).

$$C(s, \text{diamond}) \longrightarrow C(s, \text{graphite})$$

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.

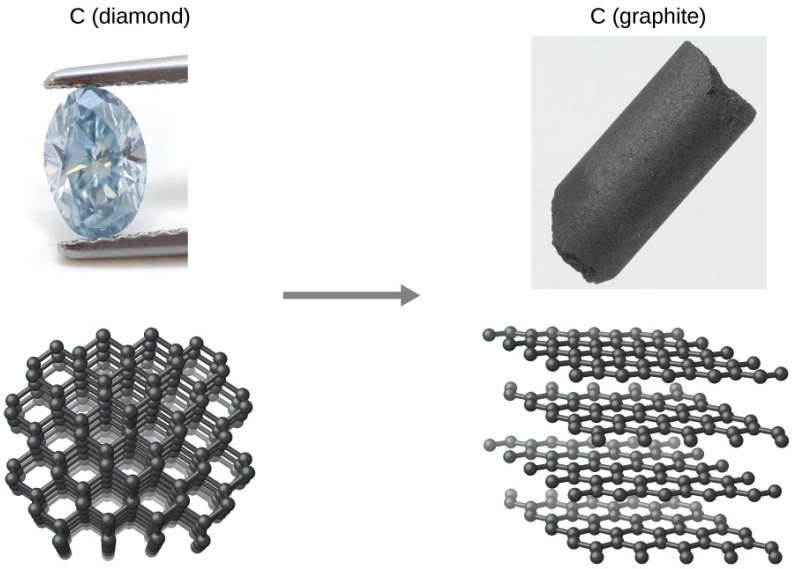


Figure 5.2.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures 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 5.2.3). 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).

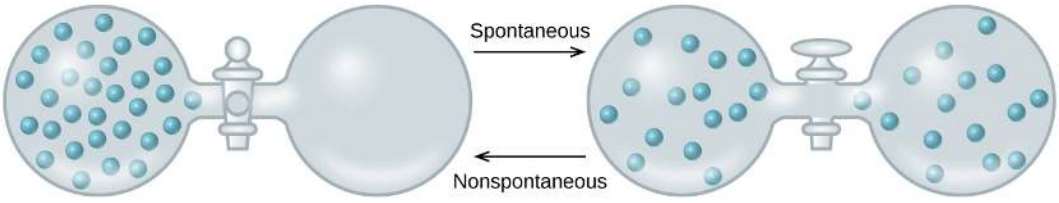


Figure 5.2.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

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 5.2.4). 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*.



Figure 5.2.4: 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 5.2.1: 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



Figure 5.2.5: (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 5.2.1

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 5.2: Spontaneity is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

5.3: 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 5.3.1) 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*.

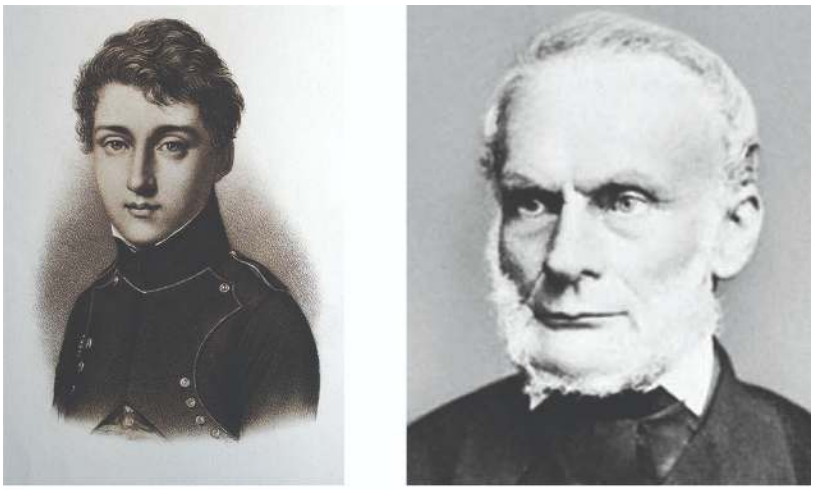


Figure 5.3.1: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

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 5.3.2. 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*.

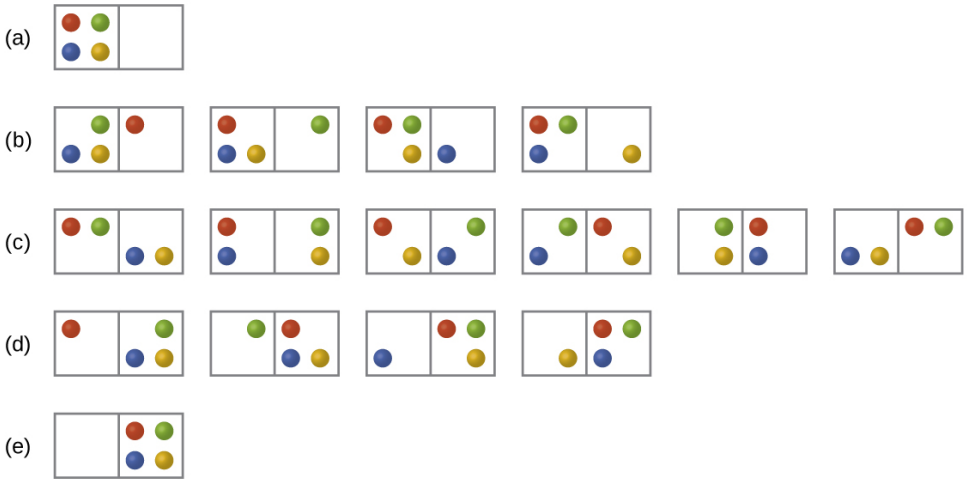


Figure 5.3.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

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 5.3.3. 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.

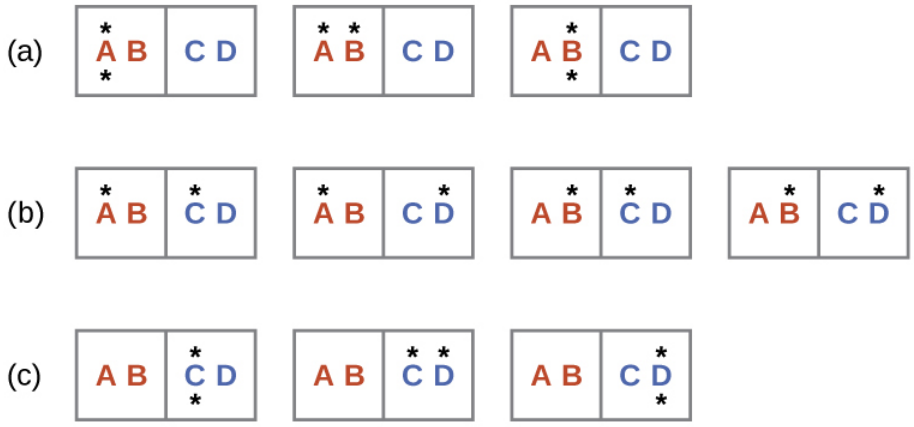
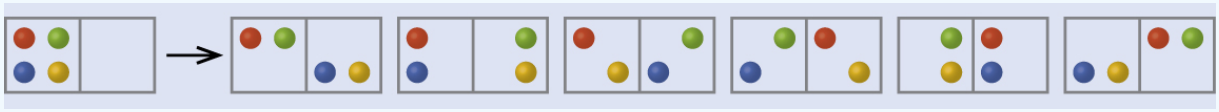


Figure 5.3.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow 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 5.3.1: 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 5.3.1

Consider the system shown in Figure 5.3.3. 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 5.3.4. 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, $\Delta S < 0$.

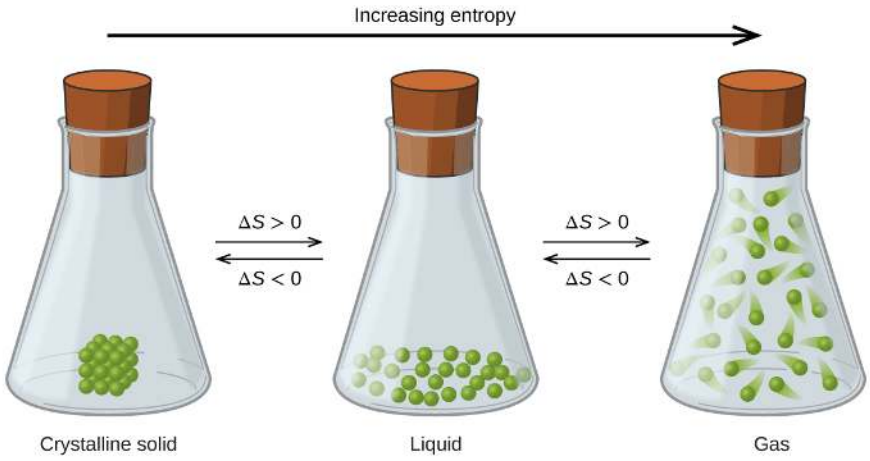


Figure 5.3.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

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 5.3.5).

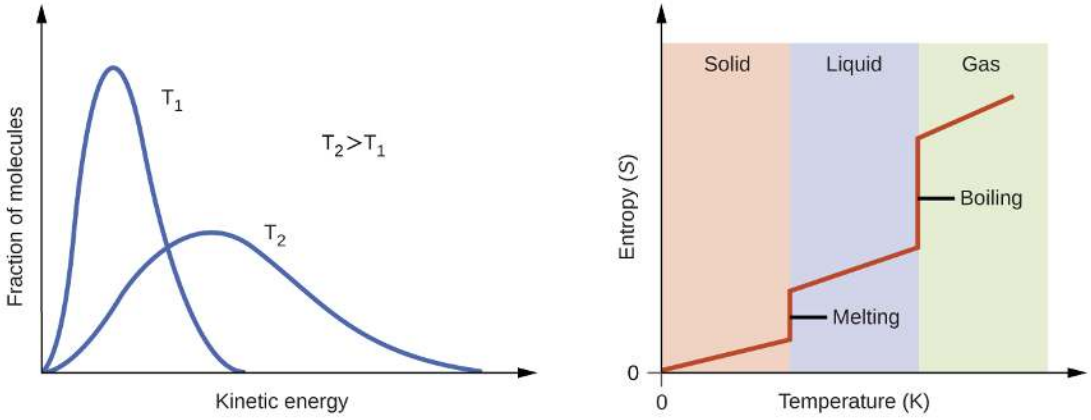


Figure 5.3.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

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 5.3.2.

Example 5.3.2: 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 5.3.1

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 5.3: Entropy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

5.4: 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 5.4.1.

Table 5.4.1: The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	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 5.4.1.

Example 5.4.1: 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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

$$= 22.1 J/K + \frac{-6.00 \times 10^3 J}{263.15 K} = -0.7 J/K$$

$S_{univ} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

$$= 22.1 J/K + \frac{-6.00 \times 10^3 J}{283.15 K} = +0.9 J/K$$

$S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

Exercise 5.4.1

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 5.4.2, 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 5.4.2: 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

Substance	($J\ mol^{-1}\ K^{-1}$)
oxygen	
$O_2(g)$	205.03

Example 5.4.2: Determination of ΔS°

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:

$$\Delta S^\circ = (1mol)\left(70.0Jmol^{-1}K^{-1}\right) - (1mol)\left(188.8Jmol^{-1}K^{-1}\right) = -118.8J/K$$

The value for Δ*S*° is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 5.4.2

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 5.4.3: 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:

$$\Delta S^\circ = \sum \nu S^\circ(\text{ products }) - \sum \nu S^\circ(\text{ reactants })$$

$$[2mol \times S^\circ(CO_2(g)) + 4mol \times S^\circ(H_2O(l))] - [2mol \times S^\circ(CH_3OH(l)) + 3mol \times S^\circ(O_2(g))]$$

$$= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\} = -161.6J/K$$

Exercise 5.4.3

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 5.4: 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.

- **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.

5.5: 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

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 5.5.1 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 5.5.1: 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, Δ*H*, and the energy lost to the surroundings, *T*Δ*S*. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, Δ*G*. 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° tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG° tells you the **extent** of a reaction. In other words, ΔG° for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^\circ < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^\circ > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

Example 5.5.1: 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:

$$\mathrm{H_2O(l) \longrightarrow H_2O(g)}$$

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	$\Delta H_f^\circ (\mathrm{kJ/mol})$	$S^\circ (\mathrm{kJ/K\ mol})$
$H_2O(l)$	−285.83	70.0
$H_2O(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ\left(\mathrm{H_2O(g)}\right) - \Delta H_f^\circ\left(\mathrm{H_2O(l)}\right)\\ &= \left[-241.82\ \mathrm{kJ/mol} - (-285.83)\right]\ \mathrm{kJ/mol} = 44.01\ \mathrm{kJ/mol}\\ \Delta S^\circ &= 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O(g)}\right) - 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O(l)}\right)\\ &= (1\ \mathrm{mol})\ 188.8 J/mol \cdot K - (1\ \mathrm{mol})\ 70.0\ \mathrm{J/mol\ K} = 118.8\ \mathrm{J\ /\ K}\\ \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\end{aligned}$$

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 5.5.1

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 Δ*G*° say about the spontaneity of this process?

$$\mathrm{C_2H_6(g) \longrightarrow H_2(g) + C_2H_4(g)}$$

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 5.5.2: Using Standard Free Energies of Formation to Calculate ΔG°

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO(s, \backslash text\{yellow\}) \longrightarrow Hg(l) + \tfrac{1}{2}O_2(g)}$$

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:

$$\begin{aligned}\Delta G^\circ &= \sum \nu G_f^\circ(\text{ products }) - \sum \nu \Delta G_f^\circ(\text{ reactants }) \\ &= \left[1\Delta G_f^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta G_f^\circ\ \mathrm{O_2(g)}\right] - 1\Delta G_f^\circ\ \mathrm{HgO(s,yellow)} \\ &= \left[1\ \mathrm{mol(0\ kJ\ /\ mol)} + \frac{1}{2}\ \mathrm{mol(0\ kJ\ /\ mol)}\right] - 1\ \mathrm{mol(-58.43\ kJ\ /\ mol)} = 58.43\ \mathrm{kJ\ /\ mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ &= \sum \nu \Delta H_f^\circ(\text{ products }) - \sum \nu \Delta H_f^\circ(\text{ reactants }) \\ &= \left[1\Delta H_f^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta H_f^\circ\ \mathrm{O_2(g)}\right] - 1\Delta H_f^\circ\ \mathrm{HgO(s,yellow)} \\ &= \left[1\ \mathrm{mol(0\ kJ\ /\ mol)} + \frac{1}{2}\ \mathrm{mol(0\ kJ\ /\ mol)}\right] - 1\ \mathrm{mol(-90.46\ kJ\ /\ mol)} = 90.46\ \mathrm{kJ\ /\ mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum \nu \Delta S^\circ(\text{ products }) - \sum \nu \Delta S^\circ(\text{ reactants }) \\ &= \left[1\ \Delta S^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta S^\circ\ \mathrm{O_2(g)}\right] - 1\Delta S^\circ\ \mathrm{HgO(s,yellow)} \\ &= \left[1\ \mathrm{mol(75.9\ J\ /\ mol\ K)} + \frac{1}{2}\ \mathrm{mol(205.2\ J\ /\ mol\ K)}\right] - 1\mathrm{mol(71.13\ J\ /\ mol\ K)} = 107.4\ \ \mathrm{J\ /\ mol\ K}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 90.46\ \mathrm{kJ} - 298.15\ \mathrm{K} \times 107.4\ \mathrm{J\ /\ K \cdot mol} \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} \\ &= (90.46 - 32.01)\ \mathrm{kJ\ /\ mol} = 58.45\ \mathrm{kJ\ /\ mol}\end{aligned}$$

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 5.5.1

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?

$$\mathrm{C_2H_4(g) \longrightarrow H_2(g) + C_2H_2(g)}$$

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:

$$\begin{array}{ll} \mathrm{H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)} & \Delta G_f^\circ \text{ gas} \\ \mathrm{H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)} & -\Delta G_f^o \text{ liquid} \\ \hline \mathrm{H_2O(l) \longrightarrow H_2O(g)} & \Delta G^\circ = \Delta G_f^\circ \text{ gas} - \Delta G_f^\circ \text{ liquid} \end{array}$$

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:

$$\mathrm{ZnS(s) \rightarrow Zn(s) + S(s)} \quad \Delta G_1^\circ = 201.3kJ$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$\mathrm{S(s) + O_2(g) \rightarrow SO_2(g)} \quad \Delta G_2^\circ = -300.1kJ$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$\mathrm{ZnS(s) + O_2(g) \rightarrow Zn(s) + SO_2(g)}$$

$$\Delta G^\circ = 201.3 \text{ kJ} + -300.1 \text{ kJ} = -98.8 \text{ kJ}$$

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 5.5.3: 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:

Decomposition of zinc sulfide:	$\mathrm{ZnS(s) \rightarrow Zn(s) + S(s)}$	$\Delta G_1^\circ = 201.3$ kJ
Formation of hydrogen sulfide:	$\mathrm{S(s) + H_2(g) \rightarrow H_2S(g)}$	$\Delta G_1^\circ = -33.4$ kJ
Coupled reaction:	$\mathrm{ZnS(s) + H_2(g) \rightarrow Zn(s) + H_2S(g)}$	$\Delta G^\circ = 201.3 \text{ kJ} + -33.4 \text{ kJ} = 167.9 \text{ kJ}$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

Exercise 5.5.3

What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?

$$\mathrm{FeS(s) + O_2(g) \rightarrow Fe(s) + SO_2(g)}$$

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° is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG° 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:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

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 5.5.1

Table 5.5.1

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.

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 5.5.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow 2\,\mathrm{CO}(g)$$

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 5.5.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s) + 3\,\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{Fe}_2\mathrm{O}_3(s)$$

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 5.5.2. 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 $\Delta G^o < 0$, $K > 1$, and the reaction will be product-favored at equilibrium. When $\Delta G^o > 0$, $K < 1$, 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 ΔG^o 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.

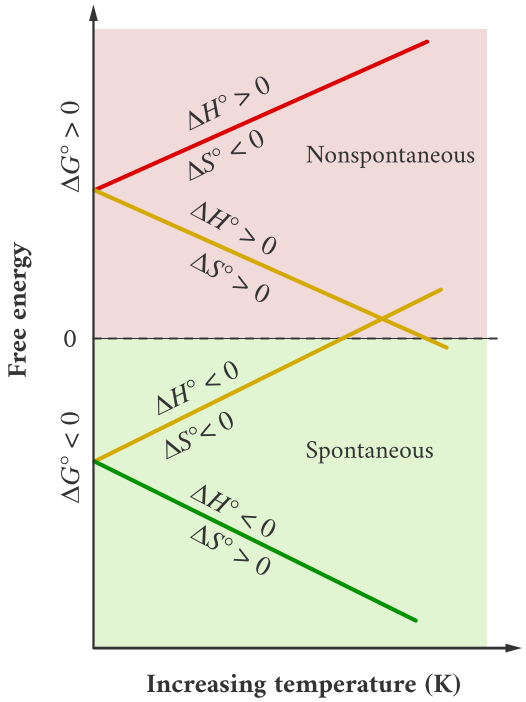


Figure 5.5.2: These plots show the variation in ΔG° with temperature for the four possible combinations of arithmetic sign for ΔH° and ΔS°. Note that in this graph of ΔG°, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 5.5.4: 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,

$$\begin{aligned}\Delta H^\circ &= \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(g)) - \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(\mathrm{H_2O}(g)) - \Delta S_{298}^\circ(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K\cdot mol} - 70.0\ \mathrm{J/K\cdot mol} = 118.8\ \mathrm{J/K\cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K\cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

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 5.5.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K).

This page titled 5.5: Free Energy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **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.

5.6: 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 (Δ*S*°) | change in entropy for a reaction calculated using the standard entropies

standard free energy change (Δ*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

---

This page titled 5.6: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

5.7: Key Equations

$$S = k \ln W$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta G = \Delta H - T\Delta S$$

This page titled 5.7: Key Equations is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

5.8: 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.

This page titled 5.8: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

5.9: Exercises

1.

What is a spontaneous reaction?

2.

What is a nonspontaneous reaction?

3.

Indicate whether the following processes are spontaneous or nonspontaneous.

(a) Liquid water freezing at a temperature below its freezing point

(b) Liquid water freezing at a temperature above its freezing point

(c) The combustion of gasoline

(d) A ball thrown into the air

(e) A raindrop falling to the ground

(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.

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.

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).

$$I_2(s) \longrightarrow I_2(g)$$

$$I_2(s) \longrightarrow I_2(l)$$

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) $Na^+(aq) + Cl^-(aq) \longrightarrow NaCl(s)$

(b) $2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_2(s)$

(c) $2C_6H_{14}(l) + 19O_2(g) \longrightarrow 14H_2O(g) + 12CO_2(g)$

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 ΔS° for the following changes.

(a) $SnCl_4(l) \longrightarrow SnCl_4(g)$

(b) $CS_2(g) \longrightarrow CS_2(l)$

(c) $Cu(s) \longrightarrow Cu(g)$

(d) $H_2O(l) \longrightarrow H_2O(g)$

(e) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

(f) $2HCl(g) + Pb(s) \longrightarrow PbCl_2(s) + H_2(g)$

(g) $Zn(s) + CuSO_4(s) \longrightarrow Cu(s) + ZnSO_4(s)$

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 $Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$. 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 S° values listed in Appendix G, calculate ΔS° for the following changes:

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

(b) $N_2(g) + \frac{5}{2}O_2(g) \longrightarrow N_2O_5(g)$

26.

From the following information, determine ΔS° for the following:

$N(g) + O(g) \longrightarrow NO(g) \qquad \Delta S^\circ = ?$

$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta S^\circ = 24.8\ \text{J/K}$

$N_2(g) \longrightarrow 2N(g) \qquad \Delta S^\circ = 115.0\ \text{J/K}$

$O_2(g) \longrightarrow 2O(g) \qquad \Delta S^\circ = 117.0\ \text{J/K}$

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.

$S^{(s)}_{\text{NaCl}} = 72.11 \frac{\text{J}}{\text{mol·K}} \qquad S^\circ_{\text{NaCl}(l)} = 95.06 \frac{\text{J}}{\text{mol·K}} \qquad \Delta H^\circ_{\text{fusion}} = 27.95\ \text{kJ/}$

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) $MnO_2(s) \longrightarrow Mn(s) + O_2(g)$

(b) $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$

(c) $Cu(s) + S(g) \longrightarrow CuS(s)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

(e) $CH_4(g) + O_2(g) \longrightarrow C(s,\ \text{graphite}) + 2H_2O(g)$

(f) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

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) $C(s,\ \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$

(b) $O_2(g) + N_2(g) \longrightarrow 2NO(g)$

(c) $2Cu(s) + S(g) \longrightarrow Cu_2S(s)$

(d) $\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$

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

(f) $\mathrm{CaSO_4 \cdot 2H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\mathrm{H_2O}(g)$

30.

What is the difference between ΔG and $\Delta G°$ for a chemical change?

31.

A reaction has ΔH° = 100 kJ/mol and $\Delta S^\circ = 250\ \mathrm{J/mol \cdot K}$. 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) $\mathrm{MnO_2}(s) \longrightarrow \mathrm{Mn}(s) + \mathrm{O_2}(g)$

(b) $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \longrightarrow 2\mathrm{HBr}(g)$

(c) $\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{CuS}(s)$

(d) $2\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g)$

(e) $\mathrm{CH_4}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{C}(s,\ \text{graphite}) + 2\mathrm{H_2O}(g)$

(f) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$

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) $\mathrm{C}(s,\ \text{graphite}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$

(b) $\mathrm{O_2}(g) + \mathrm{N_2}(g) \longrightarrow 2\mathrm{NO}(g)$

(c) $2\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{Cu_2S}(s)$

(d) $\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$

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

(f) $\mathrm{CaSO_4 \cdot 2H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\mathrm{H_2O}(g)$

35.

Given:

$\mathrm{P_4}(s) + 5\mathrm{O_2}(g) \longrightarrow \mathrm{P_4O_{10}}(s) \qquad \Delta G^\circ = -2697.0\ \mathrm{kJ/mol}$

$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{H_2O}(g) \qquad \Delta G^\circ = -457.18\ \mathrm{kJ/mol}$

$6\mathrm{H_2O}(g) + \mathrm{P_4O_{10}}(s) \longrightarrow 4\mathrm{H_3PO_4}(l) \qquad \Delta G^\circ = -428.66\ \mathrm{kJ/}$

(a) Determine the standard free energy of formation, $\Delta G_\mathrm{f}^\circ$, 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.
$2\text{HgO}(s,\text{ red}) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$

(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: $2\text{NH}_3(g) \longrightarrow \text{N}_2(g) + 3\text{H}_2(g)$

(b) Diborane: $\text{B}_2\text{H}_6(g) \longrightarrow 2\text{B}(g) + 3\text{H}_2(g)$

(c) Hydrazine: $\text{N}_2\text{H}_4(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2(g)$

(d) Hydrogen peroxide: $\text{H}_2\text{O}_2(l) \longrightarrow \text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g)$

39.

Determine ΔG^o for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:
$\text{SbCl}_5(g) \longrightarrow \text{SbCl}_3(g) + \text{Cl}_2(g)$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

(b) Chlorine molecules dissociate according to this reaction:
$\text{Cl}_2(g) \longrightarrow 2\text{Cl}(g)$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

40.

Given that the ΔG_f° 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 $PbCl_2(s)$.

41.

Determine the standard free energy change, ΔG_f°, for the formation of $S^{2-}(aq)$ given that the ΔG_f° 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}.

42.

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.

43.

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.
$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \qquad \Delta G^\circ = 8.58$

(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, P_{H_2O}, 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 P_{H_2O} in the air?

44.

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

$$\text{Glu} + \text{ATP} \longrightarrow \text{G6P} + \text{ADP} \qquad \Delta G^\circ = -17$$

In this process, ATP becomes ADP summarized by the following equation:

$$\text{ATP} \longrightarrow \text{ADP} \qquad \Delta G^\circ = -30$$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$$\text{Glu} \longrightarrow \text{G6P} \qquad \Delta G^\circ = ?$$

45.

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$$\text{G6P} \rightleftharpoons \text{F6P} \qquad \Delta G^\circ = 1.7$$

(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.

46.

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) $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$

(b) $\text{HCl}(g) + \text{NH}_3(g) \longrightarrow \text{NH}_4\text{Cl}(s)$

(c) $(\text{NH}_4)2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + 4\text{H}_2\text{O}(g) + \text{N}_2(g)$

(d) $2\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$

47.

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.

48.

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:

$$\text{Cu}_2\text{S}(s) \longrightarrow \text{Cu}(s) + \text{S}(s)$$

(a) Determine ΔG° 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 ΔG° 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.

49.

What happens to ΔG° (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) $\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$

(b) $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_3}(g)$

(c) $\mathrm{HgO}(s) \longrightarrow \mathrm{Hg}(l) + \mathrm{O_2}(g)$

This page titled 5.9: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

6: 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.

6.1: Introduction
6.2: Chemical Equilibria
6.3: Equilibrium Constants
6.4: Shifting Equilibria - Le Chatelier’s Principle
6.5: Equilibrium Calculations
6.6: Free Energy Equilibria
6.7: Key Terms
6.8: Key Equations
6.9: Summary
6.10: Exercises

This page titled 6: Fundamental Equilibrium Concepts is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

6.1: 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 6.1.1). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

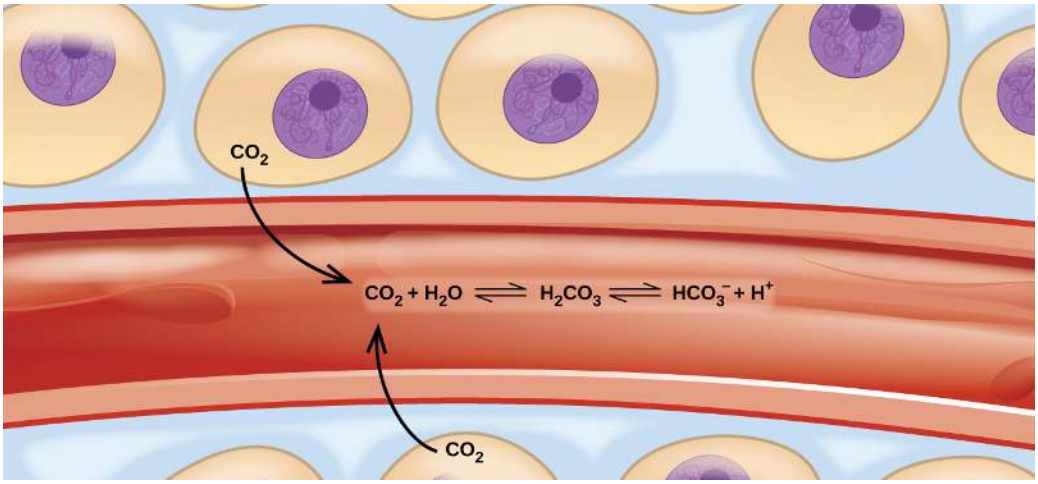


Figure 6.1.1: Transport of carbon dioxide in the body involves several reversible chemical reactions, including hydrolysis and acid ionization (among others).

This page titled 6.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

6.2: 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 $6.2.1$ 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.

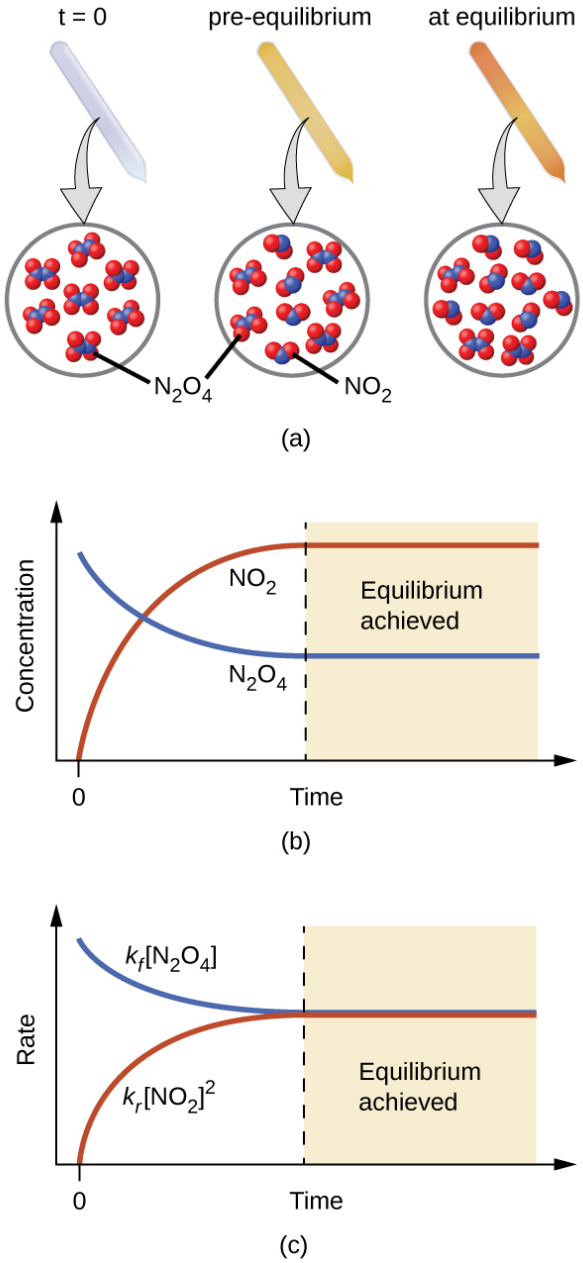


Figure 6.2.1: (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

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 6.2.1*b*). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure 6.2.1*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 6.2.1*b* and Figure 6.2.1*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.

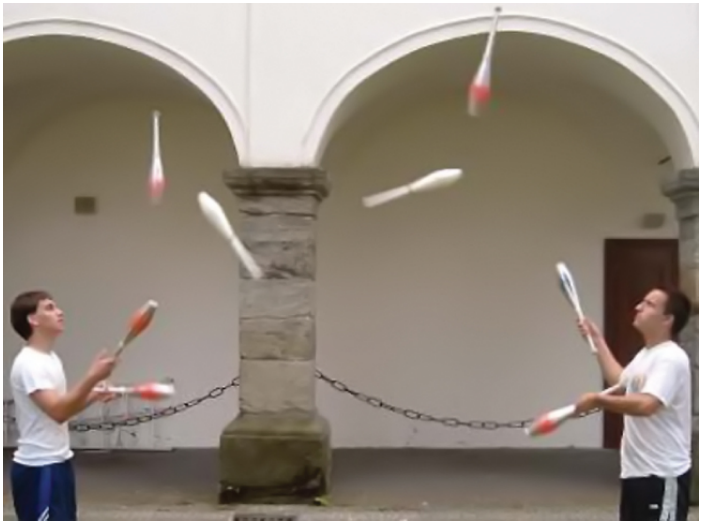


Figure 6.2.2: A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

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:

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

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 6.2.3.



Figure 6.2.3: A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

This page titled 6.2: Chemical Equilibria is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

6.3: 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 6.3.1: 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 6.3.1

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

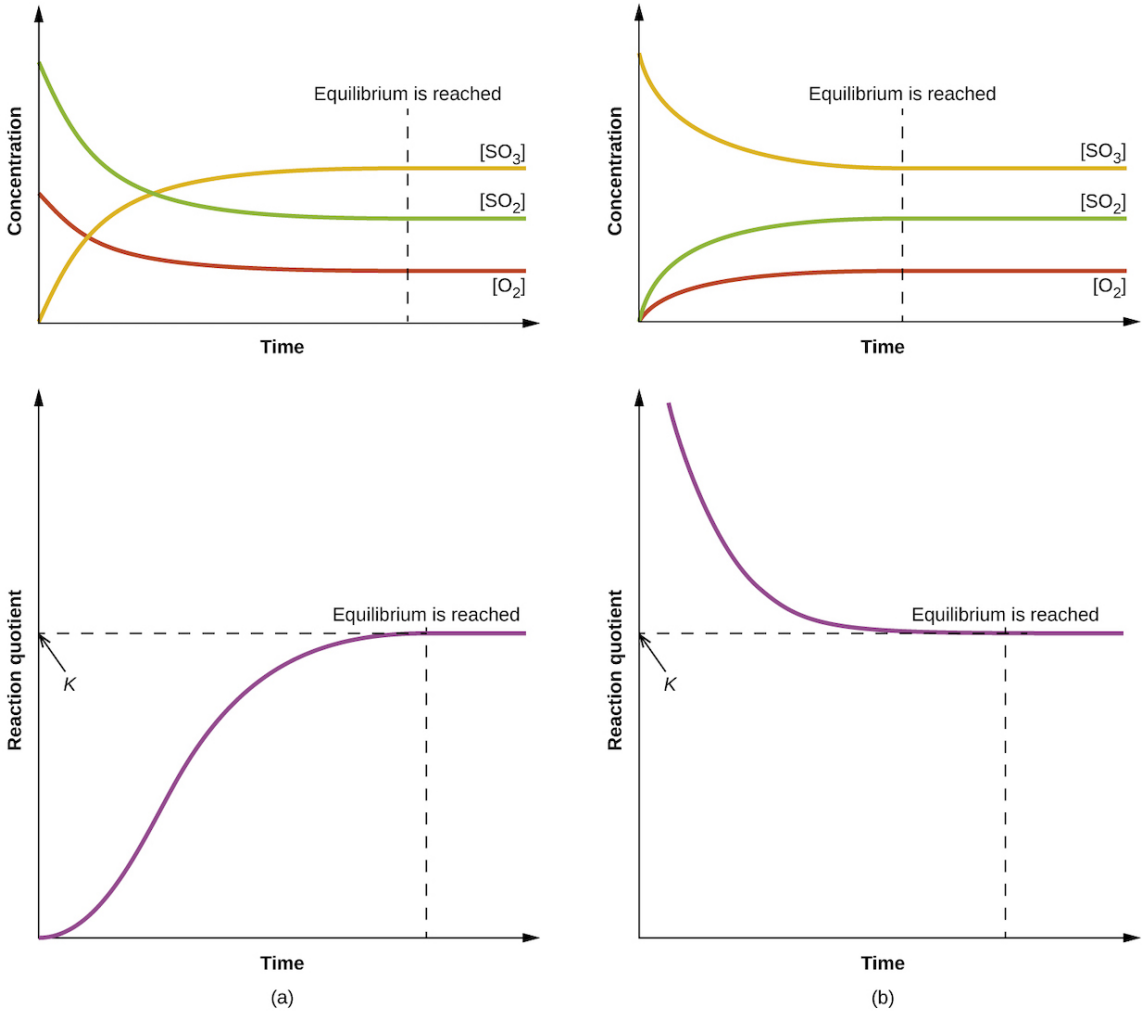


Figure 6.3.1 Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

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 6.3.1, 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:

$$Q_c = \frac{\left[\mathrm{SO_3}\right]^2}{\left[\mathrm{SO_2}\right]^2\left[\mathrm{O_2}\right]} = \frac{0^2}{\left[\mathrm{SO_2}\right]^2\left[\mathrm{O_2}\right]} = 0$$

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):

$$Q_c = \frac{\left[\mathrm{SO_3}\right]^2}{\left[\mathrm{SO_2}\right]^2\left[\mathrm{O_2}\right]} = \frac{\left[\mathrm{SO_3}\right]^2}{0} \to \infty$$

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 6.3.1 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 6.3.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,\mathrm{NO_2(g)} \rightleftharpoons \mathrm{N_2O_4(g)}$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, [NO_2] = 0.016 *M* and [N_2O_4] = 0.042 *M*.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

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

$$\left[\mathrm{NO_2}\right] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\text{ M}$$

$$\left[\mathrm{N_2O_4}\right] = 0\text{ M}$$

Thus

$$Q_c = \frac{\left[\mathrm{N_2O_4}\right]}{\left[\mathrm{NO_2}\right]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium,

$$K_c = Q_c = \frac{\left[\mathrm{N_2O_4}\right]}{\left[\mathrm{NO_2}\right]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Exercise 6.3.2

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:

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

The bar charts in Figure 6.3.2 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.

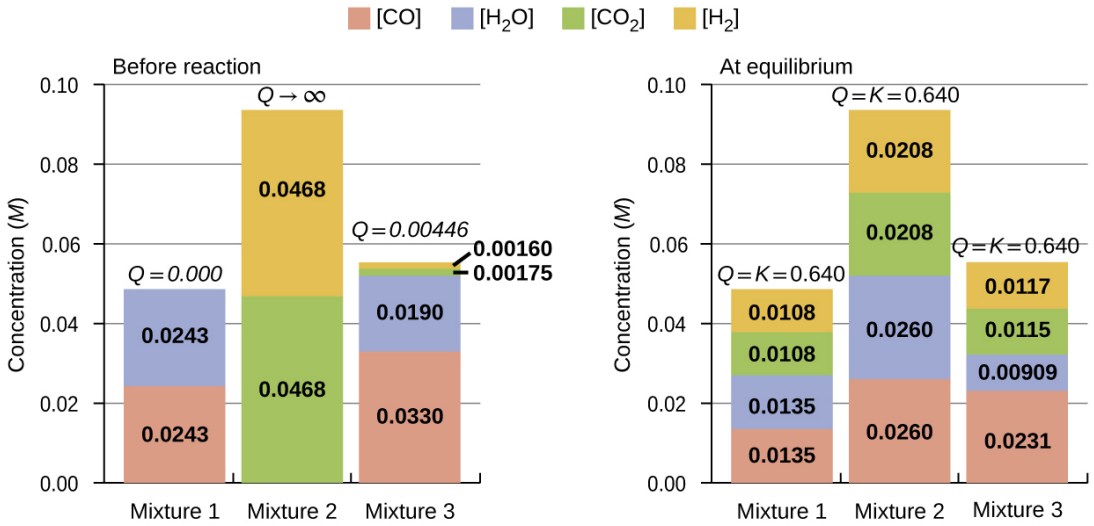


Figure 6.3.2: Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction

Example 6.3.3: 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 6.3.3

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:

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

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

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

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

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 6.3.4: 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 6.3.4

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:

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

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

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

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

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 6.3.5 demonstrates the use of this strategy in describing coupled equilibrium processes.

Example 6.3.5: Equilibrium Constants for Coupled Reactions

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

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

Use the information below to calculate Kc for this reaction.

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)}\ K_{c1} = 0.50 \text{ at } 400^\circ C$$

$$\mathrm{H_2(g)} + \mathrm{I_2(g)} \rightleftharpoons 2\,\mathrm{HI(g)}\ K_{c2} = 50 \text{ at } 400^\circ C$$

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:

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

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

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

Exercise 6.3.5

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

$$\mathrm{H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)} \qquad K_c = ?$$

$$\mathrm{CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)} \qquad K_{c1} = 490$$

$$\mathrm{CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g)} \qquad K_{c1} = 67$$

Answer

K_c = 0.14

This page titled 6.3: Equilibrium Constants is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

6.4: 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

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

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:

$$Q_P = \frac{(P_{NO})^2}{(P_{O_2})}(P_{NO_2})^2$$

$$\begin{aligned} Q'_P &= \frac{(3P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{3(P_{\mathrm{NO_2}})^2} = \frac{9(P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{9(P_{\mathrm{NO_2}})^2} = \frac{27(P_{\mathrm{NO}})^2 P_{\mathrm{O_2}}}{9(P_{\mathrm{NO_2}})^2} \\ &= 3Q_P > K_P \end{aligned}$$

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:

$$\text{dissolution} \qquad \mathrm{CO_2(g) \rightleftharpoons CO_2(aq)}$$

$$\text{hydrolysis} \qquad \mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)}$$

$$\text{ionization} \qquad \mathrm{H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)}$$

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.

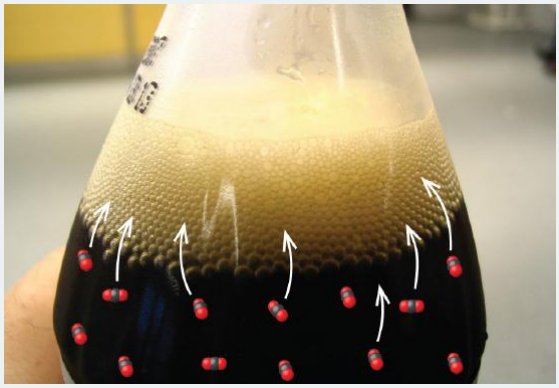


Figure 6.4.1: Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by "D Coetzee"/Flickr)

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 6.4.2. 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*.

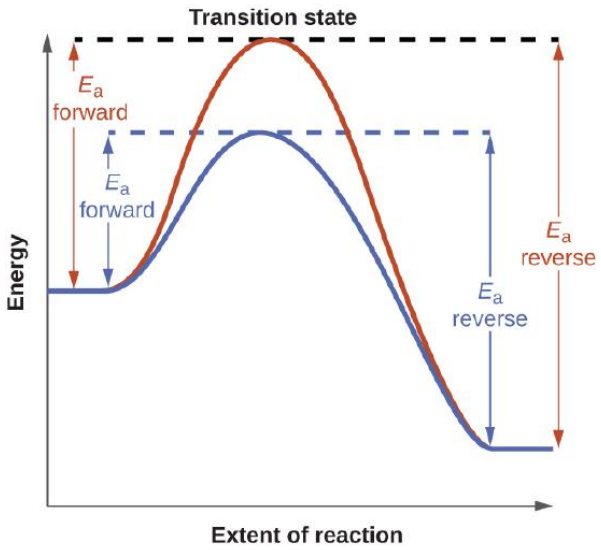


Figure 6.4.2 : Reaction diagrams for an elementary process in the absence (red) and presence (blue) of a catalyst. The presence of catalyst lowers the activation energies of both the forward and reverse reactions but does not affect the value of the equilibrium constant.

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 6.4.3.

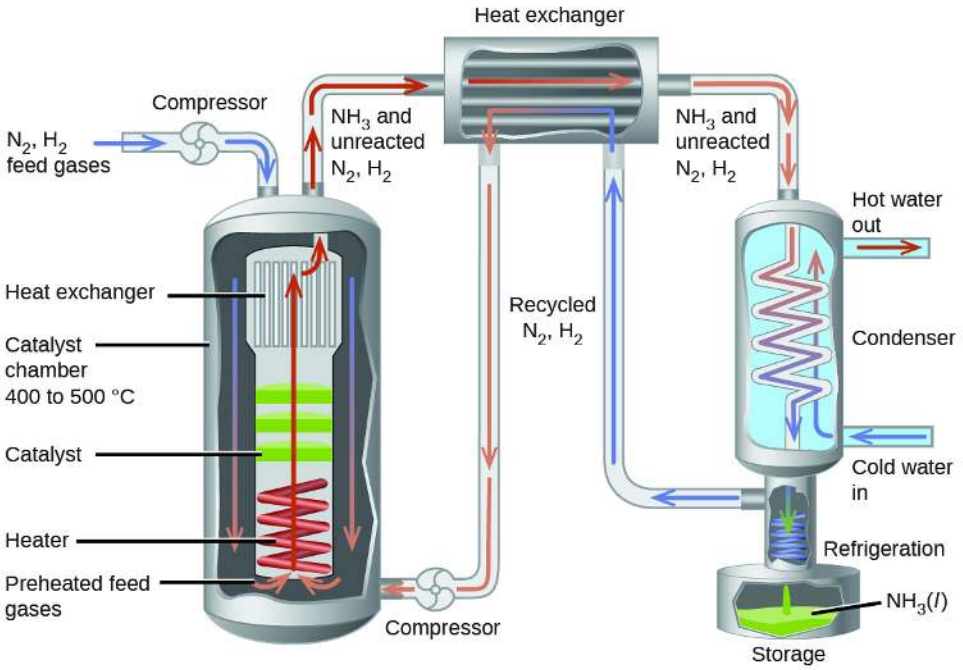


Figure 6.4.3: The figure shows a typical industrial setup for the commercial production of ammonia by the Haber-Bosch process. The process operates under conditions that stress the chemical equilibrium to favor product formation.

This page titled 6.4: Shifting Equilibria - Le Chatelier's Principle is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **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.

6.5: 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*:

$$\Delta\left[N_2\right] = +x$$

the corresponding changes in the other species concentrations are

$$\Delta\left[\mathrm{H_2}\right] = \Delta\left[\mathrm{N_2}\right]\left(\frac{3\ \mathrm{mol\ H_2}}{1\ \mathrm{mol\ N_2}}\right) = +3x$$

$$\Delta\left[\mathrm{NH_3}\right] = -\Delta\left[\mathrm{N_2}\right]\left(\frac{2\ \mathrm{mol\ NH_3}}{1\ \mathrm{mol\ N_2}}\right) = -2x$$

where the negative sign indicates a decrease in concentration.

Example 6.5.1: 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 6.5.1

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 6.5.1. 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 6.5.2: 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

$$\begin{aligned} 1.000 \times 10^{-3} - x &= 6.61 \times 10^{-4} \\ x &= 1.000 \times 10^{-3} - 6.61 \times 10^{-4} \\ &= 3.39 \times 10^{-4} M \end{aligned}$$

The ICE table may now be updated with numerical values for all its concentrations:

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the *K* expression and solve:

$$\begin{aligned} K_c &= \frac{[I_3^-]}{[I_2]\,[I^-]} \\ &= \frac{3.39 \times 10^{-4} M}{\left(6.61 \times 10^{-4} M\right)\left(6.61 \times 10^{-4} M\right)} = 776 \end{aligned}$$

? Exercise 6.5.2

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 6.5.3: 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,

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

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 6.5.3

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 6.5.4: Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant K_c for the decomposition of $\mathrm{PCl_5(g)}$ into $\mathrm{PCl_3(g)}$ and $\mathrm{Cl_2(g)}$ is 0.0211. What are the equilibrium concentrations of $\mathrm{PCl_5}$, $\mathrm{PCl_3}$, and $\mathrm{Cl_2}$ in a mixture that initially contained only $\mathrm{PCl_5}$ at a concentration of 1.00 *M*?

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

$$\begin{aligned} K_c &= \frac{\left[PCl_3\right]\left[Cl_2\right]}{\left[PCl_5\right]} = 0.0211 \\ &= \frac{(x)(x)}{(1.00 - x)} \\ 0.0211 &= \frac{(x)(x)}{(1.00 - x)} \\ 0.0211(1.00 - x)7 &= x^2 \\ x^2 + 0.0211x - 0.0211 &= 0 \end{aligned}$$

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

$$\begin{aligned}[\mathrm{PCl_5}] &= 1.00 - 0.135 = 0.87\ \mathrm{M}\\ [\mathrm{PCl_3}] &= x = 0.135\ \mathrm{M} =\\ [\mathrm{Cl_2}] &= x = 0.135\ \mathrm{M}\end{aligned}$$

Step 4.

Confirm the calculated equilibrium concentrations.

Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[\mathrm{PCl_3}]\,[\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures).

? Exercise 6.5.4A

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$\mathrm{CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O}$$

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 6.5.4B

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?

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

Answer

$[H_2]$ = 0.06 M, $[I_2]$ = 1.06 M, [HI] = 1.88 M

✓ Example 6.5.5: Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$\mathrm{HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)} \qquad K_c = 4.9 \times 10^{-10}$$

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 6.5.5

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 6.5: Equilibrium Calculations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

6.6: Free Energy Equilibria

Learning Objectives

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

- Relate standard free energy changes to equilibrium constants
- Understand how free energy relates to equilibrium positions

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 6.6.1.

Example 6.6.1: 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?

- $T = 25^\circ C$,
- $P_{N_2} = 0.870$ atm
- $P_{H_2} = 0.250$ atm
- $P_{NH_3} = 12.9$ atm

$$\Delta G^\circ = 33.0 kJ/mol$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= 33.0 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}} \times 298 K \times \ln \frac{\left(0.250^3\right) \times 0.870}{12.9^2} \right) \\ &= 9680 \frac{\text{J}}{\text{mol}} \text{ or } 9.68 \text{ kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions.

Exercise 6.6.1

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

ΔG = –123.5 kJ/mol; yes

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as

$$0 = \Delta G^\circ + RT \ln K \quad \text{(at equilibrium)}$$

$$\Delta G^\circ = -RT \ln K$$

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 6.6.1.

Table 6.6.1: Relations between Standard Free Energy Changes and Equilibrium Constants

K	$\Delta G°$	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 6.6.2: 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:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = \left[Ag^+\right]\left[Cl^-\right]$$

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:

$$K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3 J/mol}{8.314 J/mol \cdot K \times 298.15 K}\right) = \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}$$

This result is in reasonable agreement with the value provided in Appendix J.

? Exercise 6.6.2

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 6.6.1). 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.

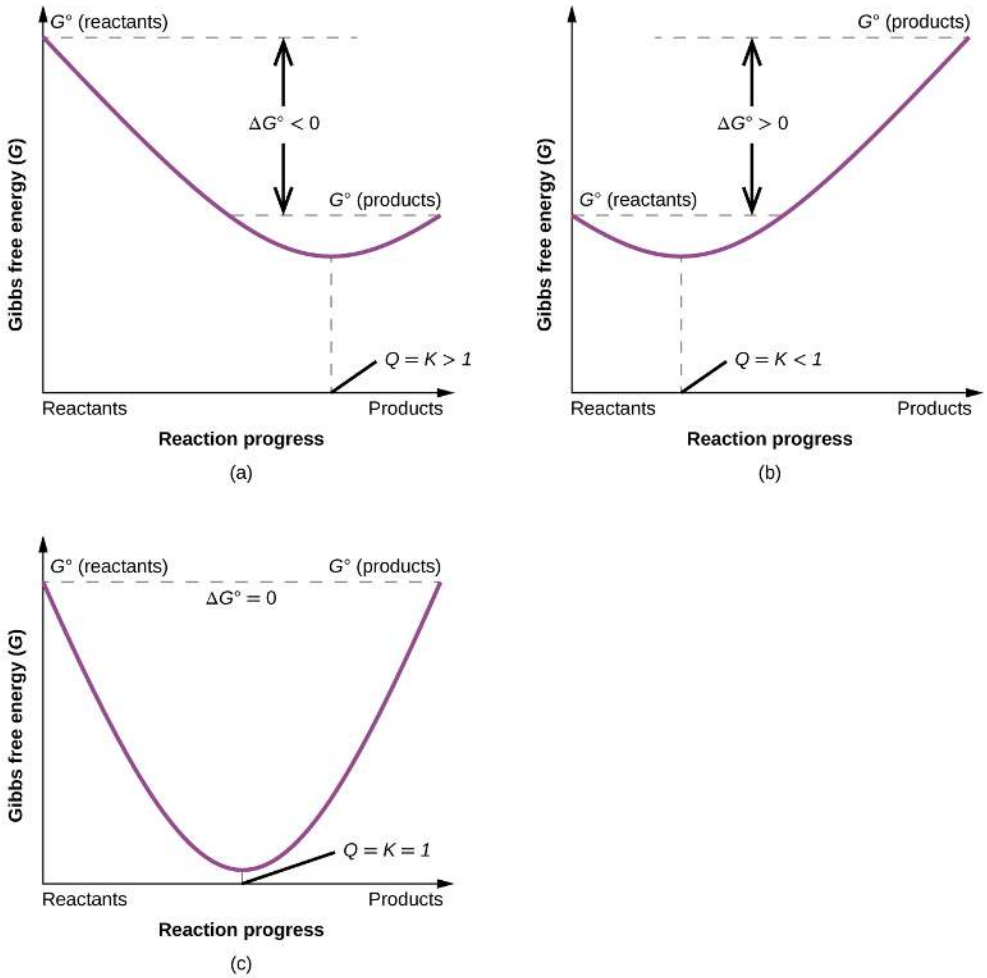


Figure 6.6.1: These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

6.6: Free Energy Equilibria is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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

6.7: 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

---

This page titled 6.7: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

6.8: Key Equations

$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]}$ for the reaction mA+nB ⇌ xC+yDQ	
$Q_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)}$ for the reaction mA+nB⇌xC+yD	
$P = MRT$	
$K_c = Q_c$ at equilibrium	
$K_p = Q_p$ at equilibrium	
$K_P = K_c\,(RT)^{\Delta n}$	
$\Delta G° = -RT\ln K$	
$\Delta G = \Delta G° + RT\ln Q$	

This page titled 6.8: Key Equations is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

6.9: 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.

This page titled 6.9: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

6.10: 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?

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

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 $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $Pb^2_+(aq) + 2Cl-(aq) \rightleftharpoons PbCl_2(s)$. 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 $CaCO_3(s) \rightleftharpoons Ca^2_+(aq) + {CO_3}^2-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $3Ba^{2+}(aq) + 2{PO_4}^{3-}(aq) \rightleftharpoons Ba_3(PO_4)_2(s)$. 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: $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

12.

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI(aq) + I_2(aq) \rightleftharpoons KI_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

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) $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

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

(d) $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$

(e) $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

(f) $Br_2(g) \rightleftharpoons 2Br(g)$

(g) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

(h) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

16.

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

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

(d) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

(e) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(f) $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$

(g) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$

(h) $S_8(g) \rightleftharpoons 8S(g)$

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) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17; [NH_3] = 0.20\ M, [N_2] = 1.00\ M, [H_2] = 1.00\ M$

(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4; NH_3 = 3.0\ \text{atm}, N_2 = 2.0\ \text{atm}, H_2 = 1.0\ \text{atm}$

(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230; [SO_3] = 0.00\ M, [SO_2] = 1.00\ M, [O_2] = 1.00\ M$

(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 16.5; SO_3 = 1.00\ \text{atm}, SO_2 = 1.00\ \text{atm}, O_2 = 1.00\ \text{atm}$

(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_c = 4.6 \times 10^4; [NO] = 1.00\ M, [Cl_2] = 1.00\ M, [NOCl] = 0\ M$

(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_P = 0.050; NO = 10.0\ \text{atm}, N_2 = O_2 = 5\ \text{atm}$

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) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17; [NH_3] = 0.50\ M, [N_2] = 0.15\ M, [H_2] = 0.12\ M$

(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4; NH_3 = 2.00\ \text{atm}, N_2 = 10.00\ \text{atm}, H_2 = 10.00\ \text{atm}$

(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230; [SO_3] = 2.00\ M, [SO_2] = 2.00\ M, [O_2] = 2.00\ M$

(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 6.5\ \text{atm}; SO_2 = 1.00\ \text{atm}, O_2 = 1.130\ \text{atm}, SO_3 = 0\ \text{atm}$

(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_P = 2.5 \times 10^3; NO = 1.00\ \text{atm}, Cl_2 = 1.00\ \text{atm}, NOCl = 0\ \text{atm}$

(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.050; [N_2] = 0.100\ M, [O_2] = 0.200\ M, [NO] = 1.00\ M$

19.

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

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

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52 atm

20.

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

$[SO_2Cl_2]$ = 0.12 *M*, $[Cl_2]$ = 0.16 *M* and $[SO_2]$ = 0.050 *M*. K_c for the reaction is 0.078.

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) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.50$ at 400 °C
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_c = 50.2$ at 448 °C
(c) $Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$ $K_P = 4.08 \times 10^{-}25$ at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.122$ at 50 °C

26.

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

(a) $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$ $K_c = 4.7 \times 10^{-}2$at 25 °C
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_P = 48.2$ at 500 °C
(c) $CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g)$ $K_P = 5.09 \times 10^{-}44$at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.196$ at 60 °C

27.

What is the value of the equilibrium constant expression for the change $H_2O(l) \rightleftharpoons H_2O(g)$

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 $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (The equilibrium vapor pressure for this substance is 570 torr at 25 °C.)

31.

The following equation represents a reversible decomposition:
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

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:
$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

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

(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(b) Is the reaction endothermic or exothermic?

36.

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:
$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad \Delta H =$

37.

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:
$P_4(g) + 6H_2(g) \rightleftharpoons 4PH_3(g) \qquad \Delta H = 110.5\ \text{kJ}$

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) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad \Delta H =$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H =$

(c) $2O_3(g) \rightleftharpoons 3O_2(g) \qquad \Delta H = -$

(d) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad \Delta H = -$

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) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \qquad \Delta H = 484\ \text{kJ}$

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.2\ \text{kJ}$

(c) $2Br(g) \rightleftharpoons Br_2(g) \qquad \Delta H = -224\ \text{kJ}$

(d) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g) \qquad \Delta H =$

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
$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.2\ \text{kJ}$

(b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

(c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

41.

Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181\ \text{kJ}$

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the 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?

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
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H = 131.30\ \text{kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

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
$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2Fe(s) + 3H_2O(g) \qquad \Delta H = 98.7\ \text{kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the 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:
$NH_3(aq) + H_2O(l) \rightleftharpoons {NH_4}^+(aq) + {OH}^-(aq)$

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH

(b) Addition of HCl

(c) Addition of NH_4Cl

45.

Acetic acid is a weak acid that reacts with water according to this equation:
$CH_3CO_2H(aq) + H_2O(aq) \rightleftharpoons H_3O{+}(aq) + {CH_3CO_2}^-(aq)$

Will any of the following increase the percent of acetic acid that reacts and produces ${CH_3CO_2}^-$ ion?

(a) Addition of HCl

(b) Addition of NaOH

(c) Addition of $NaCH_3CO_2$

46.

Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and $NO_3{}^-$, in contact with solid AgCl.

$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3{}^-(aq) \rightleftharpoons AgCl(s) + Na^+(aq) + NO_3{}^-(aq)$

$\Delta H = -65.9\ \text{kJ}$

47.

How can the pressure of water vapor be increased in the following equilibrium?

$H_2O(l) \rightleftharpoons H_2O(g)$ $\Delta H =$

48.

A solution is saturated with silver sulfate and contains excess solid silver sulfate:

$Ag_2SO_4(s) \rightleftharpoons 2Ag+(aq) + SO_4{}^2-(aq)$

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: $A(aq) + 2B(aq) \rightleftharpoons 2C(aq)$ $K_c = 1 \times 10^3$

(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: $2W(aq) \rightleftharpoons X(aq) + 2Y(aq)$ $K_c = 5 \times 10^{-4}$

(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?

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

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

53.

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

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.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

56.

Calculate the value of the equilibrium constant K_P for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ 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:

$$I_2(g) \rightleftharpoons 2I(g)$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

58.

A sample of ammonium chloride was heated in a closed container.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

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?

$$H_2O(l) \rightleftharpoons H_2O(g)$$

60.

Complete the following partial ICE tables.

(a)

	$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g)+$	$O_2(g)$
change	___		___	$+x$

(b)

	$4NH_3(g)$	$+3O_2(g)$	$\rightleftharpoons$	$2N_2(g)+$	$6H_2O(g)$
change	___	$+x$		___	___

(c)

	$2CH_4(g)$	$\rightleftharpoons$	$C_2H_2(g)+$	$3H_2(g)$
change	___		$+x$	___

(d)

	$CH_4(g)+$	$H_2O(g)$	$\rightleftharpoons$	$CO(g)+$	$3H_2(g)$
change	___	$+x$		___	___

(e)

	$NH_4Cl(s)$	$\rightleftharpoons$	$NH_3(g)+$	$HCl(g)$
change		$+x$	___	

(f)

	$Ni(s)+$	$4CO(g)$	$\rightleftharpoons$	$Ni(CO)_4(g)$
change	$+x$		___	

61.

Complete the following partial ICE tables.

(a)

	$2H_2(g)+$	$O_2(g)$	$\rightleftharpoons$	$2H_2O(g)$
change	___	___		$+x$

(b)

	$CS_2(g)+$	$4H_2(g)$	$\rightleftharpoons$	$CH_4(g)+$	$2H_2S(g)$
change	$+x$	___		___	___

(c)

	$H_2(g)+$	$Cl_2(g)$	$\rightleftharpoons$	$2HCl(g)$
change	$+x$	___		___

(d)

	$2NH_3(g)$	$+2O_2(g)$	$\rightleftharpoons$	$N_2O(g)+$	$3H_2O(g)$
change	___	___		___	$+x$

(e)

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)+$	$H_2S(g)$
change		$+x$	___	

(f)

	$Fe(s)+$	$5CO(g)$	$\rightleftharpoons$	$Fe(CO)_5(g)$
change		___		$+x$

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*.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ ^\circ C$

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.

$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ C$

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?

$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad K_P = 4.7 \times 10^{-2}$

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?

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad K_P = 1.6 \text{ at } 990\ ^\circ C$

68.

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \qquad K_c = 4.90 \times 10^2 \text{at } 550\ ^\circ C$

What concentration of CO remains in an equilibrium mixture with [CO_2] = 0.100 *M*?

69.

Carbon reacts with water vapor at elevated temperatures.

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad K_c = 0.2 \text{ at } 1000\ ^\circ C$

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

$Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \qquad K_P = 4.08 \times 10^{-25} \text{ at } 25\ ^\circ C$

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

$CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \qquad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ C$

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:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_c = 4.32$

What are the equilibrium concentrations of all species in a mixture that was prepared with [SO_3] = 0.500 *M*, [SO_2] = 0 *M*, and [O_2] = 0.350 *M*?

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*?

$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = 160$

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.

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 1.07 \times 10^{-}$ 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*.

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g) \qquad K_c = 2.2 \times 10^{-10}$

(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.

$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g) \qquad K_P = 2.2 \times 10^{-6}$

(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?

$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K_c = 0.0900$

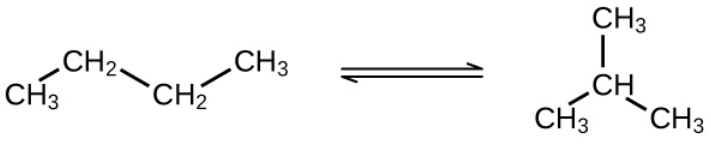
78.

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ C$

79.

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?

80.

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?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

81.

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

82.

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

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

(a) How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?

(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

83.

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water 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.

84.

Antimony pentachloride decomposes according to this equation:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

85.

Consider the equilibrium

$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$

(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?

(c) If the reaction were at equilibrium, how would 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?

86.

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

$$HbO_2(aq) + H_3O^+(aq) + CO_2(g) \rightleftharpoons CO_2\text{–}Hb\text{–}H^+ + O_2(g) + H_2O(l)$$

(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.

87.

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 $NO(g)$.

88.

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

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

89.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g) \qquad \Delta G^\circ = -10.88\ \text{kJ}$

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g) \qquad \Delta G^\circ = 3.4\ \text{kJ}$

(c) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g) \qquad \Delta G^\circ = -39\ \text{kJ}$

(d) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta G^\circ = -141.82\ \text{kJ}$

(e) $CS_2(g) \longrightarrow CS_2(l) \qquad \Delta G^\circ = -1.88\ \text{kJ}$

90.

Calculate the equilibrium constant at the temperature given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2F_2O(g) \qquad (\text{T} = 100\ ^\circ\text{C})$

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g) \qquad (\text{T} = 0.0\ ^\circ\text{C})$

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g) \qquad (\text{T} = 575\ ^\circ\text{C})$

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \qquad (\text{T} = -10.0\ ^\circ\text{C})$

(e) $SnCl_4(l) \longrightarrow SnCl_4(g) \qquad (\text{T} = 200\ ^\circ\text{C})$

91.

Calculate the equilibrium constant at the temperature given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g) \qquad (\text{T} = 100\ ^\circ\text{C})$

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g) \qquad (\text{T} = 0.0\ ^\circ\text{C})$

(c) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g) \qquad (\mathrm{T} = 125\ ^\circ\mathrm{C})$

(d) $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{SO_3}(g) \qquad (\mathrm{T} = 675\ ^\circ\mathrm{C})$

(e) $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l) \qquad (\mathrm{T} = 90\ ^\circ\mathrm{C})$

92.

Consider the following reaction at 298 K:
$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g) \qquad K_P = 0.142$

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.

93.

Determine the normal boiling point (in kelvin) of dichloroethane, $\mathrm{CH_2Cl_2}$. 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.

94.

Under what conditions is $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g)$ spontaneous?

95.

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.)

96.

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2\mathrm{H_2S}(g) + \mathrm{SO_2}(g) \rightleftharpoons \frac{3}{8}\mathrm{S_8}(s,\ \text{rhombic}) + 2\mathrm{H_2O}(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

97.

Consider the decomposition of $\mathrm{CaCO_3}(s)$ into $\mathrm{CaO}(s)$ and $\mathrm{CO_2}(g)$. What is the equilibrium partial pressure of $\mathrm{CO_2}$ at room temperature?

98.

In the laboratory, hydrogen chloride ($\mathrm{HCl}(g)$) and ammonia ($\mathrm{NH_3}(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($\mathrm{NH_4Cl}(s)$), 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 $\mathrm{NH_3}$ in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

99.

Benzene can be prepared from acetylene. $3\mathrm{C_2H_2}(g) \rightleftharpoons \mathrm{C_6H_6}(g)$. 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?

100.

Carbon dioxide decomposes into CO and $\mathrm{O_2}$ at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of $\mathrm{CO_2}$ was 1.15 atm?

101.

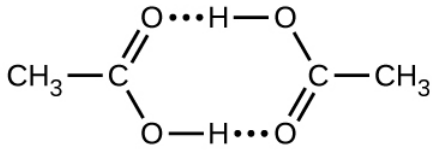
Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.
$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$

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?

102.

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.
$2CH_3CO_2H(g) \longrightarrow (CH_3CO_2H)_2(g)$

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?

103.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	$T = 2000\ ^\circ C$	$K_p = 4.1 \times 10^{-4}$
(b) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$	$T = 400\ ^\circ C$	$K_p = 50.0$
(c) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$	$T = 980\ ^\circ C$	$K_p = 1.67$
(d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	$T = 900\ ^\circ C$	$K_p = 1.04$
(e) $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq)$	$T = 25\ ^\circ C$	$K_p = 7.2 \times 10^{-4}$
(f) $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$	$T = 25\ ^\circ C$	$K_p = 3.3 \times 10^{-13}$

104.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $Cl_2(g) + Br_2(g) \longrightarrow 2BrCl(g)$	$T = 25\ ^\circ C$	$K_p = 4.7 \times 10^{-2}$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$T = 500\ ^\circ C$	$K_p = 48.2$
(c) $H_2O(l) \rightleftharpoons H_2O(g)$	$T = 60\ ^\circ C$	$K_p = 0.196$
(d) $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$	$T = 550\ ^\circ C$	$K_p = 4.90 \times 10^2$
(e) $CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3{}^+(aq) + OH^-(aq)$	$T = 25\ ^\circ C$	$K_p = 4.4 \times 10^{-4}$
(f) $PbI_2(s) \longrightarrow Pb^2{+}(aq) + 2I^-(aq)$	$T = 25\ ^\circ C$	$K_p = 8.7 \times 10^{-9}$

105.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$	$\Delta G^\circ = -9.2\ kJ$
(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$	$\Delta G^\circ = 7.3\ kJ$
(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$	$\Delta G^\circ = -79\ kJ$
(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$	$\Delta G^\circ = -1.6\ kJ$
(e) $SnCl_4(l) \longrightarrow SnCl_4(l)$	$\Delta G^\circ = 8.0\ kJ$

This page titled 6.10: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

7: 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.

7.1: Introduction
7.2: Brønsted-Lowry Acids and Bases
7.3: pH and pOH
7.4: Relative Strengths of Acids and Bases
7.5: Hydrolysis of Salt
7.6: Polyprotic Acids
7.7: Buffers
7.8: Acid-Base Titrations
7.9: Key Terms
7.10: Key Equations
7.11: Summary
7.12: Exercises

This page titled 7: Acid-Base Equilibria is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

7.1: Introduction

Liquid water is essential to life on our planet, and chemistry involving the characteristic ions of water, H^+ and 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 H^+ transfer reactions are reversible, and the equilibria established by acid-base systems are essential aspects of phenomena ranging from sinkhole formation (Figure 7.1.1) 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 7.1.1: 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)

This page titled 7.1: Introduction is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

- **14.0: Introduction** is licensed CC BY 4.0.

7.2: Brønsted-Lowry Acids and Bases

Learning Objectives

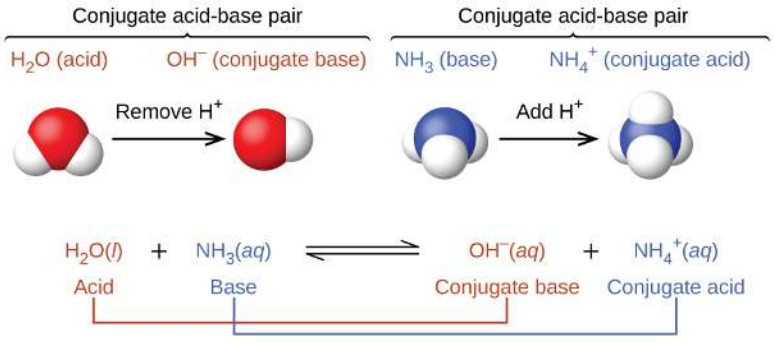
By the end of this section, you will be able to:

- 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

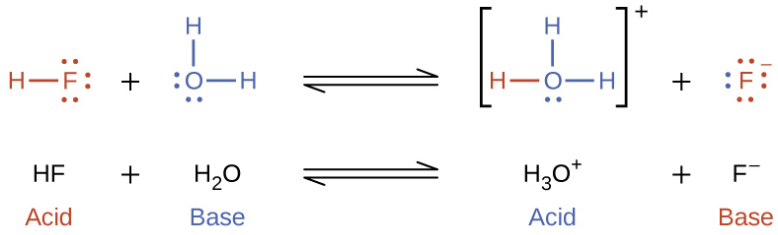
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. 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).

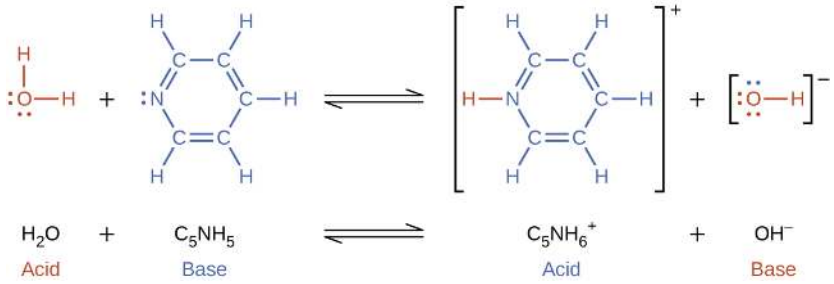
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, 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:



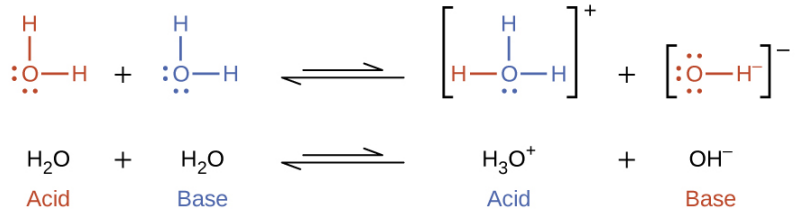
The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called amphiprotic, or more generally, amphoteric, a term that may be 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:

$$\mathrm{HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)}$$

$$\mathrm{HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)}$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents 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:

$$\mathrm{2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)} \tag{7.2.1}$$

with

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{7.2.2}$$

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 7.2.1: 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:

$$K_w = \left[H_3O^+\right]\left[OH^-\right] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

So:

$$x = \left[H_3O^+\right] = \left[OH^-\right] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, $1.0 \times 10^{-7}\ M$.

Exercise 7.2.1

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

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = 4.9 \times 10^{-7}\ M$$

Example 7.2.2: 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 7.2.1 and 7.2.2) to calculate the missing equilibrium concentration.

$$2\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq) + OH^-(aq)}$$

with $K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}]$.

Rearrangement of the K_w expression shows that [OH^-] is inversely proportional to [H_3O^+]:

$$K_w = \left[\mathrm{H_3O^+}\right]\left[\mathrm{OH^-}\right] = \left(2.0 \times 10^{-6}\right)\left(5.0 \times 10^{-9}\right) = 1.0 \times 10^{-14}$$

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:

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 7.2.2

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 7.2.3: 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 7.2.3

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 7.2: Brønsted-Lowry Acids and Bases is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **14.1: Brønsted-Lowry Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.3: 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:

$$pH = -\log\left[H_3O^+\right]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$\left[H_3O^+\right] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$pOH = -\log\left[OH^-\right]$$

or

$$\left[OH^-\right] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_w &= \left[\mathrm{H_3O^+}\right]\left[\mathrm{OH^-}\right] \\ -\log K_w &= -\log\left(\left[\mathrm{H_3O^+}\right]\left[\mathrm{OH^-}\right]\right) \\ &= -\log\left[\mathrm{H_3O^+}\right] + -\log\left[\mathrm{OH^-}\right] \\ pK_w &= pH + pOH \end{aligned} \tag{7.3.1}$$

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:

$$pH = -\log\left[H_3O^+\right] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

$$pOH = -\log\left[OH^-\right] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

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 7.3.1 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 7.3.1).

Table 7.3.1: 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 7.3.1: shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

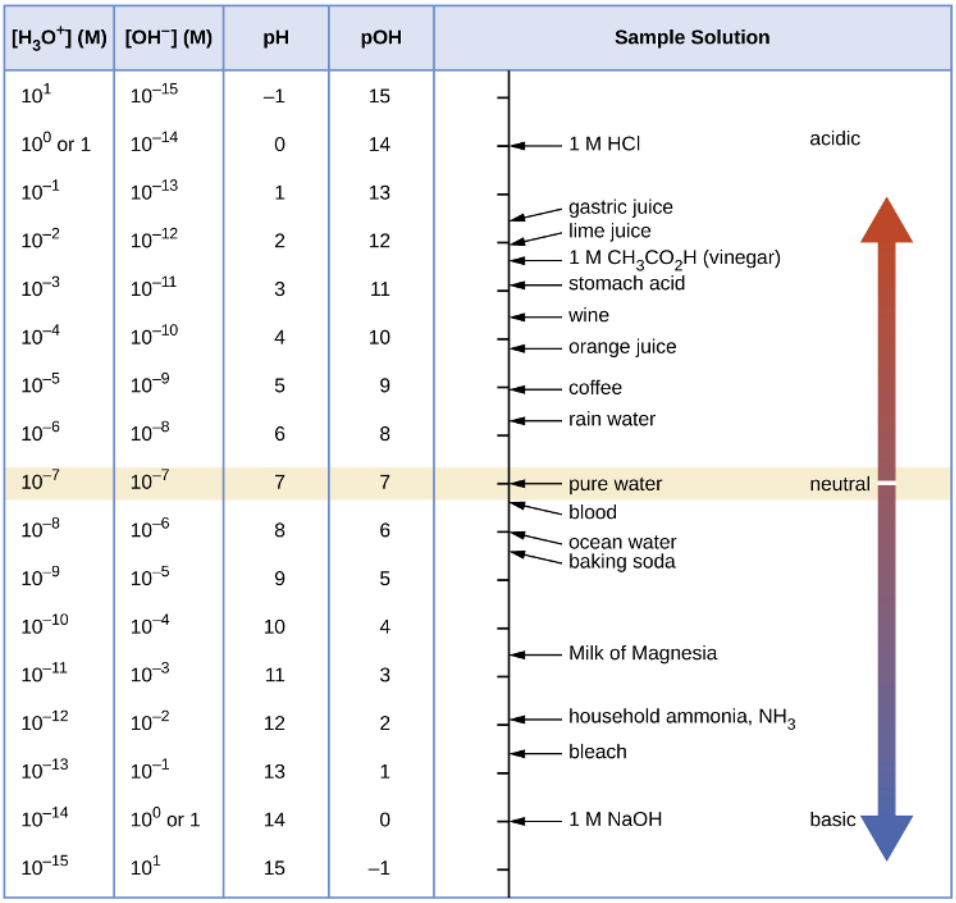


Figure 7.3.1: The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

Example 7.3.1: Calculation of pH from [H_3O^+]

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log\left[\mathrm{H_3O^+}\right] \\ &= -\log\left(1.2 \times 10^{-3}\right) \\ &= -(-2.92) = 2.92 \end{aligned}$$

(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 7.3.1

Water exposed to air contains carbonic acid, $\mathrm{H_2CO_3}$, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved $\mathrm{CO_2}$ of 2.0×10^{-6} M, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 7.3.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned} pH = -\log\left[H_3O^+\right] &= 7.3 \\ \log\left[H_3O^+\right] &= -7.3 \\ \left[H_3O^+\right] &= 10^{-7.3} \end{aligned}$$

or

$$\begin{aligned} [\mathrm{H_3O^+}] &= \text{antilog of } -7.3 \\ &= 5 \times 10^{-8} M \end{aligned}$$

(On a calculator take the antilog, or the “inverse” log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 7.3.2

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 $\mathrm{CO_2}$ which forms carbonic acid:

$$\mathrm{H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq)}$$

$$\mathrm{H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)}$$

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 7.3.2). 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 7.3.2: (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 ✔ 7.3.3: 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*:

$$\text{pOH} = -\log\left[OH^-\right] = -\log 0.0125$$
$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\begin{aligned} \text{pH} + \text{pOH} &= 14.00 \\ pH &= 14.00 - pOH \\ &= 14.00 - 1.903 = 12.10 \end{aligned}$$

? Exercise 7.3.3

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 7.3.3).



(a) (b)

Figure 7.3.3: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 7.3.4). 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 7.3.4: (a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

This page titled 7.3: pH and pOH is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **14.2: pH and pOH** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.4: 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 7.4.1.

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 7.4.1: 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:

$$\mathrm{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)}$$

the acid ionization constant is written

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[\mathrm{H_2O}]$ 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 $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ 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:

$$\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$$

as demonstrated with the equations below:

$$\mathrm{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)} \qquad K_a = 4.6 \times 10^{-4}$$

$$\mathrm{HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)} \qquad K_a = 1.2 \times 10^{-2}$$

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:

$$\%\ \text{ionization} = \frac{\left[\mathrm{H_3O^+}\right]_{eq}}{[\mathrm{HA}]_0} \times 100$$

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 7.4.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{\left[\mathrm{H_3O^+}\right]_{eq}}{\left[\mathrm{HNO_2}\right]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$\left[\mathrm{H_3O^+}\right] = 10^{-2.09} = 0.0081M$$

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 7.4.1

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

$$K_b = \frac{\left[\mathrm{HB^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{B}\right]}$$

Inspection of the data for three weak bases presented below shows the base strength increases in the order: $\mathrm{NO_2^-} < \mathrm{CH_2CO_2^-} < \mathrm{NH_3}$

$$\mathrm{NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)} \qquad K_b = 2.17 \times 10^{-11}$$

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)} \qquad K_b = 5.6 \times 10^{-10}$$

$$\mathrm{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)} \qquad K_b = 1.8 \times 10^{-5}$$

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

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

and

$$\mathrm{A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq)}$$

with

$$K_b = \frac{[\mathrm{HA}][\mathrm{OH-}]}{[\mathrm{A-}]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\mathrm{\cancel{HA(aq)} + H_2O(l) + \cancel{A^-(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \cancel{A^-(aq)} + OH^-(aq) + \cancel{HA(aq)}}$$

$$\mathrm{2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)}$$

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 7.4.2: illustrates this relation for several conjugate acid-base pairs.

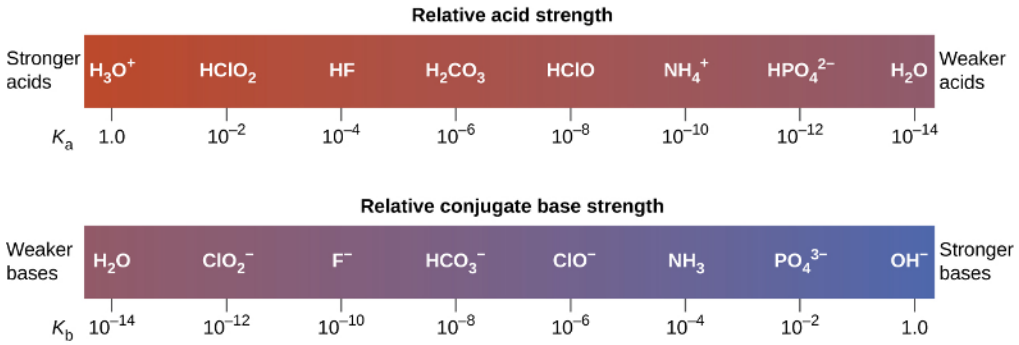


Figure 7.4.2: Relative strengths of several conjugate acid-base pairs are shown.

The listing of conjugate acid–base pairs shown in Figure 7.4.3: 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.

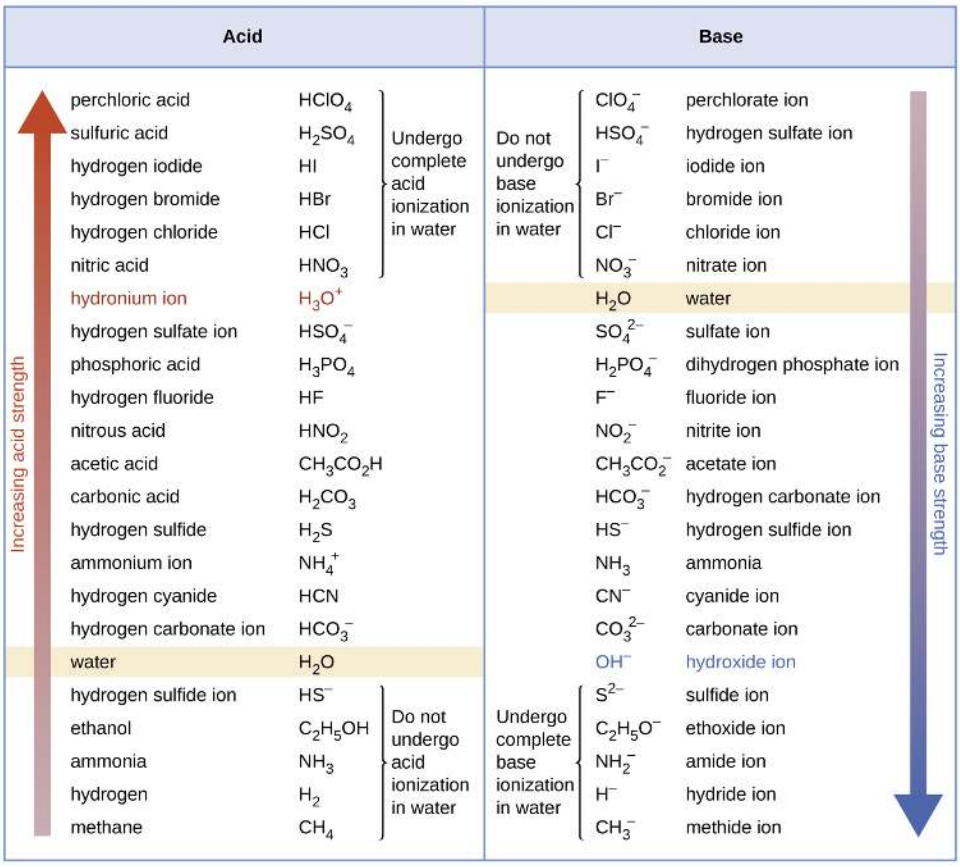


Figure 7.4.3: This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

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 7.4.3 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 7.4.2: 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 7.4.2

Determine the relative acid strengths of $NH4^+$ 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 $NH4^+$ 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 7.4.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 7.4.4) 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 7.4.4: 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.

$$\mathrm{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)}$$

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{CH_3CO_2^-}\right]}{\left[\mathrm{CH_3CO_2H}\right]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

? Exercise 7.4.3

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 7.4.4: 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 7.4.4

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: $[OH^-] = 1.3 \times 10^{-6}\,M$; $H_2PO_4^-] = 0.042\,M$; and $[HPO_4^{2-}] = 0.341\,M$?

Answer

K_b for HPO_4^{2-} is 1.6×10^{-7}

Example 7.4.5: 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:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ \text{M}$$

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 7.4.5

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 7.4.6: 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 7.4.5).



Figure 7.4.5: 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?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

The ICE table for this system is

	HCO_2H +	H_2O ⇌	H_3O^+ +	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

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

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:

$$x = [H_3O^+] = 0.0098 \text{ M}$$

Finally, the pH is calculated to be

$$\text{pH} = -\log\left[\text{H}_3\text{O}^+\right] = -\log(0.0098) = 2.01$$

Exercise 7.4.6

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?

$$\text{CH}_3\text{CO}_2\text{H(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{CH}_3\text{CO}_2^-\text{(aq)} \quad K_a = 1.8 \times 10^{-5}$$

Answer

percent ionization = 1.3%

Example 7.4.7: 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:

$$(\text{CH}_3)_3\text{N(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+\text{(aq)} + \text{OH}^-\text{(aq)} \quad K_b = 6.3 \times 10^{-5}$$

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:

$$\begin{aligned}\left[OH^-\right] &= \sim 0 + x \\ &= x = 4.0 \times 10^{-3} M\end{aligned}$$

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 7.4.7

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 7.4.8 below.

Example 7.4.8: 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

$$K_a = 1.2 \times 10^{-2} = \frac{\left[H_3O^+\right]\left[SO_4^{2-}\right]}{\left[HSO_4^-\right]} = \frac{(x)(x)}{0.50 - x}$$

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:

$$\frac{x}{\left[HSO_4^-\right]_i}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

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.

$$x = \left[H3O^+\right] = 0.072 \text{ M}$$

$$\text{pH} = -\log\left[\text{H}_3\text{O}^+\right] = -\log(0.072) = 1.14$$

? Exercise 7.4.8

Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\text{C}_8\text{H10 N}_4\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_8\text{H10 N}_4\text{O}_2\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_b = 2.5 \times 10^{-4}$$

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

$$\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}\cdot$$

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 7.4.6).

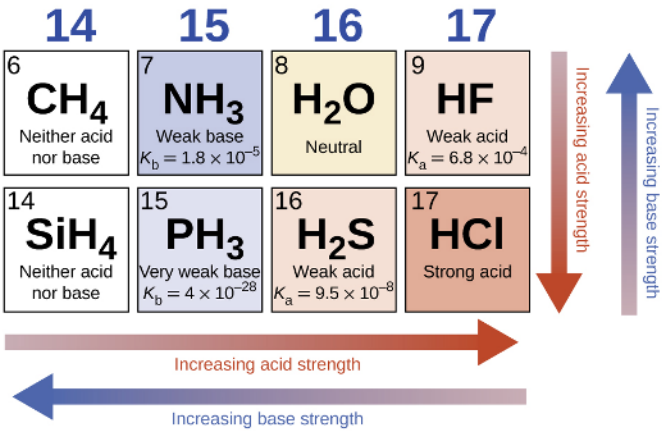
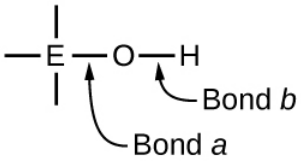


Figure 7.4.6: The figure shows trends in the strengths of binary acids and bases.

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 7.4.7).

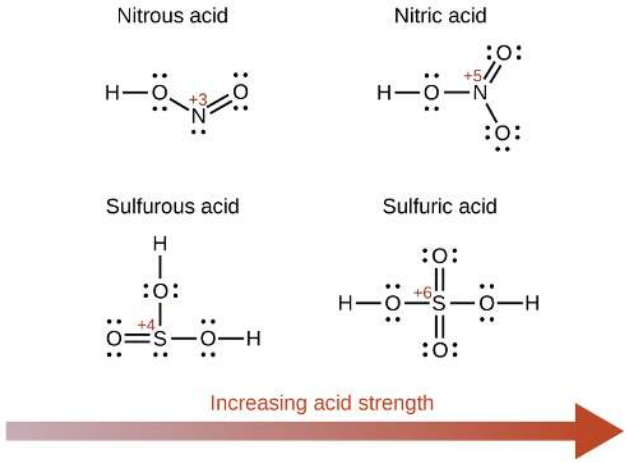


Figure 7.4.7: As the oxidation number of the central atom E increases, the acidity also increases.

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 $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$Al(H_2O)_3(OH)_3(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ 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 $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3\,H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6^{3+}(aq) + 3\,H_2O(l)$$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

This page titled 7.4: Relative Strengths of Acids and Bases is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **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.

7.5: Hydrolysis of Salt

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 7.5.1: 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

$$K_a = \frac{\left[\mathrm{C_6H_5NH_2}\right]\left[\mathrm{H_3O^+}\right]}{\left[\mathrm{C_6H_5NH_3^+}\right]}$$

$$2.3 \times 10^{-5} = \frac{(x)(x)}{0.233 - x}$$

Assuming $x \ll 0.233$, the equation is simplified and solved for x:

$$2.3 \times 10^{-5} = \frac{x^2}{0.233}$$

$$x = 0.0023\ \mathrm{M}$$

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

$$\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right] = -\log(0.0023) = 2.64$$

? Exercise 7.5.1

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, $\mathrm{NH_4NO_3}$, a salt composed of the ions NH_4^+ and NO_3^- and.

Which is the stronger acid $\mathrm{C_6H_5NH_3^+}$ or $\mathrm{NH_4^+}$?

Answer

$[\mathrm{H_3O^+}] = 7.5 \times 10^{-6}\ \mathrm{M}$; is the stronger acid.

Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

$$\mathrm{NaCH_3CO_2(s) \rightleftharpoons Na^+(aq) + CH_3CO_2^-(aq)}$$

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, $\mathrm{CH_3CO_2^-(aq)}$, is the conjugate base of acetic acid, $\mathrm{CH_3CO_2H}$, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH{-}(aq)} \quad K_b = K_w/K_a$$

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 ($\mathrm{Na^+}$) and weak base anions ($\mathrm{CH_3CO_2^-}$), resulting in a basic solution.

✓ Example 7.5.2: 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 $[\mathrm{OH^-}] = 0.050\ \mathrm{M}$ and $[\mathrm{OH^-}] = 2.5 \times 10^{-6} M$ at equilibrium. The reaction is:

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)}$$

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

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)}$$

Substituting the available values into the K_b expression gives

$$K_b = \frac{[CH_3CO_2H]\left[\mathrm{OH^-}\right]}{\left[\mathrm{CH_3CO_2^-}\right]} = 5.6 \times 10^{-10}$$

$$= \frac{\left[\mathrm{CH_3CO_2H}\right]\left(2.5 \times 10^{-6}\right)}{(0.050)} = 5.6 \times 10^{-10}$$

Solving the above equation for the acetic acid molarity yields $\left[\mathrm{CH_3CO_2H}\right] = 1.1 \times 10^{-5}\ \mathrm{M}$.

? Exercise 7.5.2

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 7.5.3: 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 $\mathrm{K^+}$ 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 $\mathrm{Na^+}$ cation is inert and will not affect the pH of the solution; while the $\mathrm{HCO_3^-}$ anion is amphiprotic. The K_a of $\mathrm{HCO_3^-}$ 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 $\mathrm{Na^+}$ cation is inert and will not affect the pH of the solution, while the $\mathrm{HPO_4^{2-}}$ anion is amphiprotic. The K_a of $\mathrm{HPO_4^{2-}}$ 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 $\mathrm{NH_4^+}$ ion is acidic (see above discussion) and the $\mathrm{F^-}$ ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of $\mathrm{NH_4^+}$ is 5.6 × 10−10 and the K_b of $\mathrm{F^-}$ is 1.6×10^{-11}, so the solution is acidic, since $K_a > K_b$.

? Exercise 7.5.3

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 7.5.1, 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.

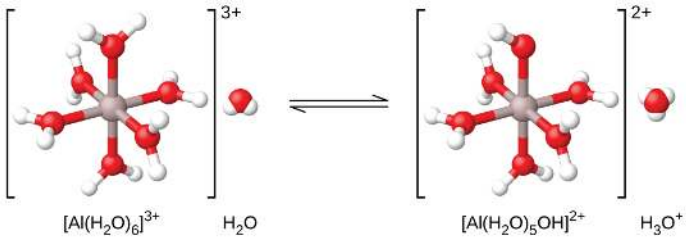


Figure 7.5.1: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

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:

$$\mathrm{Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Fe(H_2O)_5(OH)^{2+}(aq)} \qquad pK_a = 2.74$$

$$\mathrm{Cu(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cu(H_2O)_5(OH)^{+}(aq)} \qquad pK_a = \sim 6.3$$

$$\mathrm{Zn(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Zn(H_2O)_3(OH)^{+}(aq)} \qquad pK_a = 9.6$$

Example 7.5.4: 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 ($\mathrm{[Al(H_2O)_6]^{3+}}$) in solution.

Solution

The equation for the reaction and K_a are:

$$\mathrm{Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq)} \qquad K_a = 1.4 \times 10^{-5}$$

An ICE table with the provided information is

	$\mathrm{Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{2+}}$		
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:

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{Al(H_2O)_5(OH)^{2+}}\right]}{\left[\mathrm{Al(H_2O)_6^{3+}}\right]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Assuming $x \ll 0.10$ and solving the simplified equation gives:

$$x = 1.2 \times 10^{-3}\ \mathrm{M}$$

The ICE table defined x as equal to the hydronium ion concentration, and so the pH is calculated to be

$$\mathrm{[H_3O^+]} = 0 + x = 1.2 \times 10^{-3}\ \mathrm{M}$$

$$\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right] = 2.92$$

Therefore this is an acidic solution.

Exercise 7.5.4

What is $\mathrm{[Al(H_2O)_5(OH)^{2+}]}$ in a 0.15-M solution of $\mathrm{Al(NO_3)_3}$ that contains enough of the strong acid $\mathrm{HNO_3}$ to bring [$\mathrm{H_3O^+}$] to 0.10 *M*?

Answer

$2.1 \times 10^{-5} M$

This page titled 7.5: Hydrolysis of Salt is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **14.4: Hydrolysis of Salt Solutions** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.6: Polyprotic Acids

Learning Objectives

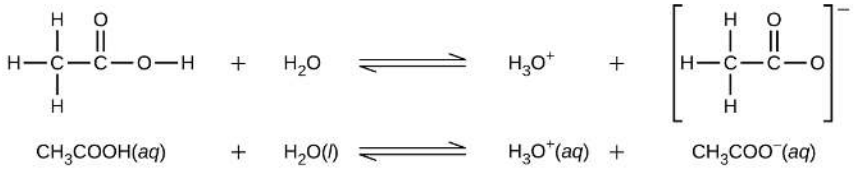
By the end of this section, you will be able to:

- 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 HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$
$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

Even though it contains four hydrogen atoms, acetic acid, CH_3CO_2H, is also monoprotic because only the hydrogen atom from the carboxyl group ($-COOH$) 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:

$$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq) \qquad \text{(First ionization)}$$

with $K_{a1} > 10^2$.

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad \text{(Second ionization)}$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. Carbonic acid, 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.

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad \text{(First ionization)}$$

with

$$K_{H_2CO_3} = \frac{\left[H_3O^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad \text{(Second ionization)}$$

with

$$K_{HCO_3^-} = \frac{\left[H_3O^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the

concentrations of H_3O^+ and are practically equal in a pure aqueous solution of 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 7.6.1: 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?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11}$$

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

Using provided information, an ICE table for this first step is prepared:

	H_2CO_3 +	H_2O ⇌	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:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

$$K_{HCO_3^-} = \frac{[H3O^+]\,[CO_3^{2-}]}{[HCO_3^-]} = \frac{(1.2 \times 10^{-4})\,[CO_3^{2-}]}{1.2 \times 10^{-4}}$$

$$[CO_3^{2-}] = \frac{(4.7 \times 10^{-11})\,(1.2 \times 10^{-4})}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11}M$$

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 7.6.1

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:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \quad K_{a1} = 7.5 \times 10^{-3} \qquad \text{(First ionization)}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \quad K_{a2} = 6.2 \times 10^{-8} \qquad \text{(Second ionization)}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \quad K_{a3} = 4.2 \times 10^{-13} \qquad \text{(Third ionization)}$$

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 7.6: Polyprotic Acids is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

7.7: 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 7.7.1). 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 7.7.1: (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):

$$\mathrm{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)}$$

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 7.7.2 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.

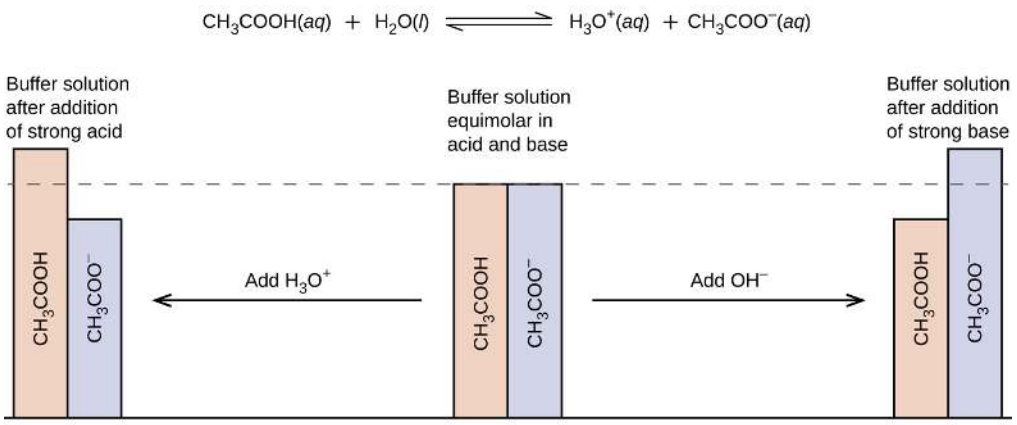


Figure 7.7.2: Buffering action in a mixture of acetic acid and acetate salt.

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

$$x = 1.8 \times 10^{-5}\ \text{M}$$

$$\left[\text{H}_3\text{O}^+\right] = 0 + x = 1.8 \times 10^{-5}\ \text{M}$$

$$pH = -\log\left[\text{H}_3\text{O}^+\right]$$

$$= -\log\left(1.8 \times 10^{-5}\right)$$

$$= 4.74$$

(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.

$$0.0010\ \cancel{\text{L}} \times \left(\frac{0.10\ \text{mol NaOH}}{1\ \text{L}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

The initial molar amount of acetic acid is

$$0.100 \cancel{\text{ L}} \times \left(\frac{0.100 \text{ mol } CH_3CO_2H}{1 \cancel{\text{ L}}} \right) = 1.00 \times 10^{-2} \text{ mol } CH_3CO_2H$$

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:

$$\left[CH_3CO_2H\right] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \text{ M}$$

$$\left[NaCH_3CO_2\right] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \text{ M}$$

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

$$\left[H_3O^+\right] = 10^{-4.74} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{mol } H_3O^+ = (0.100 \text{ L})\left(1.8 \times 10^{-5} \text{ M}\right) = 1.8 \times 10^{-6} \text{ mol } H_3O^+$$

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

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\,H_2O(l)$$

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 7.7.1

Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a 1.8×10^{-5} M HCl solution from 4.74 to 3.00.

Answer

Initial pH of 1.8×10^{-5} 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:

$$pH = -\log\left[\text{H}_3\text{O}^+\right] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4} mol + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}\right) = 3.00$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 7.7.3). 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 7.7.3: 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 7.7.4 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.

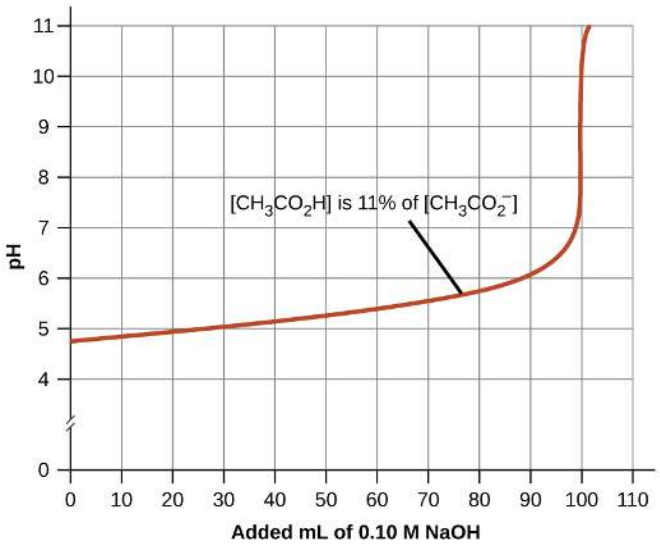


Figure 7.7.4: Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H]$ = 0.10 *M* and Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH 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, H_2CO_3, and the bicarbonate ion, HCO_3^-. When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

An added hydroxide ion is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

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:

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$ yields:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

Taking the negative logarithm of both sides of this equation gives

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

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

where pK_a is the negative of the logarithm of the ionization constant of the weak acid (pK_a = −log K_a). 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 7.7: Buffers is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

7.8: 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 7.8.1: 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 7.8.1). 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:

$$\left[\mathrm{H_3O^+}\right] = \frac{n\left(\mathrm{H^+}\right)}{V} = \frac{0.002500\ \mathrm{mol} \times \left(\frac{1000\ mL}{1\ L}\right) - 0.100\ M \times 12.50\ mL}{25.00\ mL + 12.50\ mL} = 0.0333\ M$$

(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:

$$n\left(OH^-\right)_0 > n\left(H^+\right)_0$$

$$\left[\mathrm{OH}^-\right]=\frac{n\left(\mathrm{OH}^-\right)}{\mathrm{V}}=\frac{0.100\ \mathrm{M}\times 37.50\ \mathrm{mL}-0.002500\ \mathrm{mol}\times\left(\frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}\right)}{25.00\ \mathrm{mL}+37.50\ \mathrm{mL}}=0.0200\ \mathrm{M}$$

$$\mathrm{pH}=14-\mathrm{pOH}=14+\log([\mathrm{OH}^-])=14+\log(0.0200)=12.30$$

Exercise 7.8.1

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 7.8.2: 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:

$$\mathrm{CH_3CO_2H+OH^-\longrightarrow CH_3CO_2^-+H_2O}$$

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:

$$K_a=\frac{[H3O^+]\left[CH_3CO_2^-\right]}{[CH_3CO_2H]}\approx\frac{[H3O^+]^2}{[CH_3CO_2H]_0}$$

and

$$\left[H3O^+\right]=\sqrt{K_a\times[CH_3CO_2H]}=\sqrt{1.8\times10^{-5}\times0.100}=1.3\times10^{-3}$$

$$pH=-\log\left(1.3\times10^{-3}\right)=2.87$$

(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

$$\frac{0.00250\ \mathrm{mol}}{0.0500\ \mathrm{L}}=0.0500\ \mathrm{M}\ \mathrm{CH_3CO_2^-}$$

Base ionization of acetate is represented by the equation

$$\mathrm{CH_3CO_2^-(aq)+H_2O(l)\rightleftharpoons CH_3CO_2H(aq)+OH^-(aq)}$$

$$K_b=\frac{[H^+]\left[OH^-\right]}{K_a}=\frac{K_w}{K_a}=\frac{1.0\times10^{-14}}{1.8\times10^{-5}}=5.6\times10^{-10}$$

Assuming $x\ll0.0500$, the pH may be calculated via the usual ICE approach:

$$K_b=\frac{x^2}{0.0500M}$$

$$x=\left[OH^-\right]=5.3\times10^{-6}$$

$$\text{pOH} = -\log\left(5.3 \times 10^{-6}\right) = 5.28$$
$$\text{pH} = 14.00 - 5.28 = 8.72$$

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:

$$pH = pK_a + \log\frac{[\text{ Base }]}{[\text{ Acid }]} = -\log(K_a) + \log\frac{\left[\text{CH}_3\text{CO}_2^-\right]}{\left[\text{CH}_3\text{CO}_2\text{H}\right]} = -\log\left(1.8 \times 10^{-5}\right) + \log(1)$$
$$pH = -\log\left(1.8 \times 10^{-5}\right) = 4.74$$

(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:

$$\left[\text{OH}^-\right] = \frac{(0.003750mol - 0.00250mol)}{0.06250L} = 2.00 \times 10^{-2}M$$
$$\text{pOH} = -\log\left(2.00 \times 10^{-2}\right) = 1.70$$
$$\text{pH} = 14.00 - 1.70 = 12.30$$

? Exercise 7.8.1

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 7.8.1 and plotted as titration curves in Figure 7.8.1. 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 7.8.1: 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

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]
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

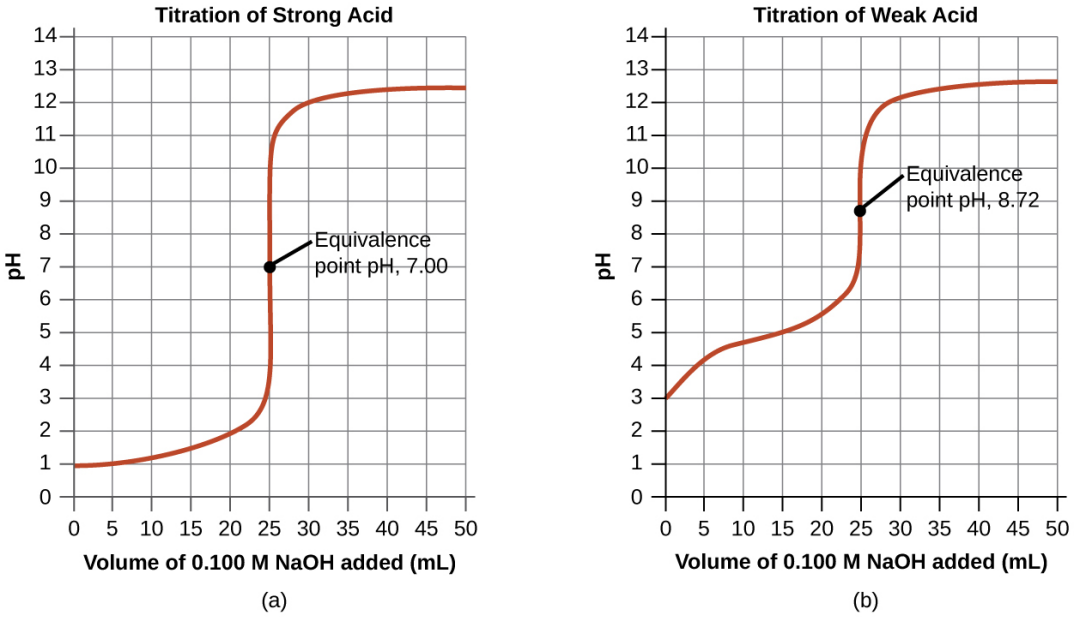


Figure 7.8.1: (a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an 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:

$$\underset{\text{red}}{\mathrm{HIn(aq)}} + \mathrm{H_2O(l)} \rightleftharpoons \underset{\text{yellow}}{\mathrm{H_3O^+(aq)}} + In^-(aq)$$

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{In^-}\right]}{\left[\mathrm{HIn}\right]} = 4.0 \times 10^{-4}$$

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):

$$pH = pKa + \log\left(\frac{\left[\mathrm{In^-}\right]}{\left[\mathrm{HIn}\right]}\right)$$

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 $7.8.2$ presents several indicators, their colors, and their color-change intervals.

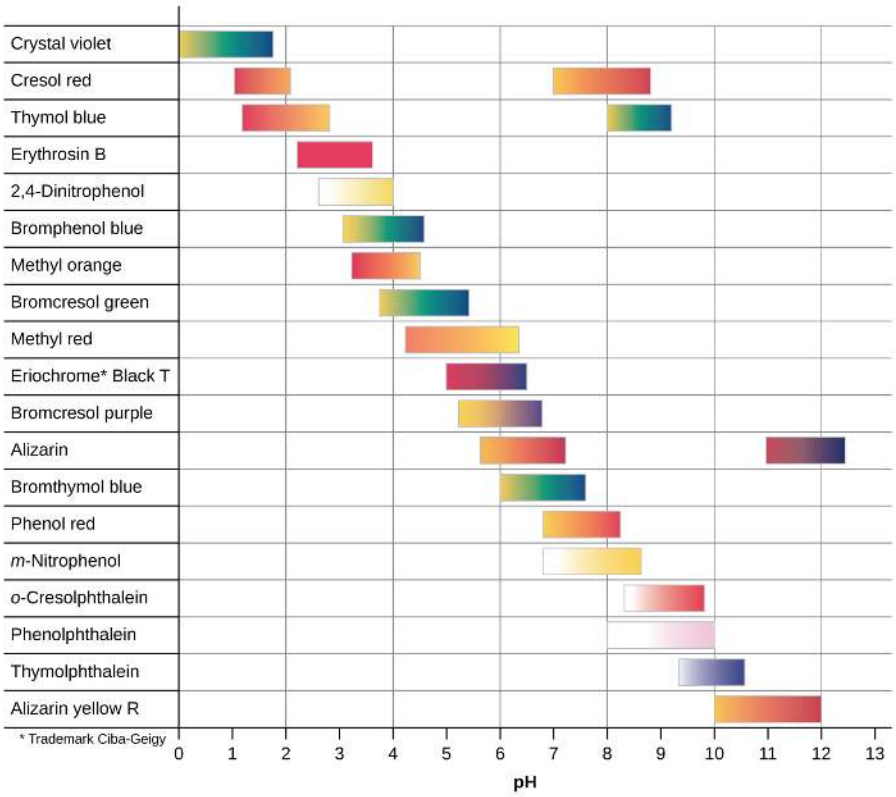


Figure 7.8.2: This chart illustrates the color change intervals for several acid-base indicators.

The titration curves shown in Figure 7.8.3 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.

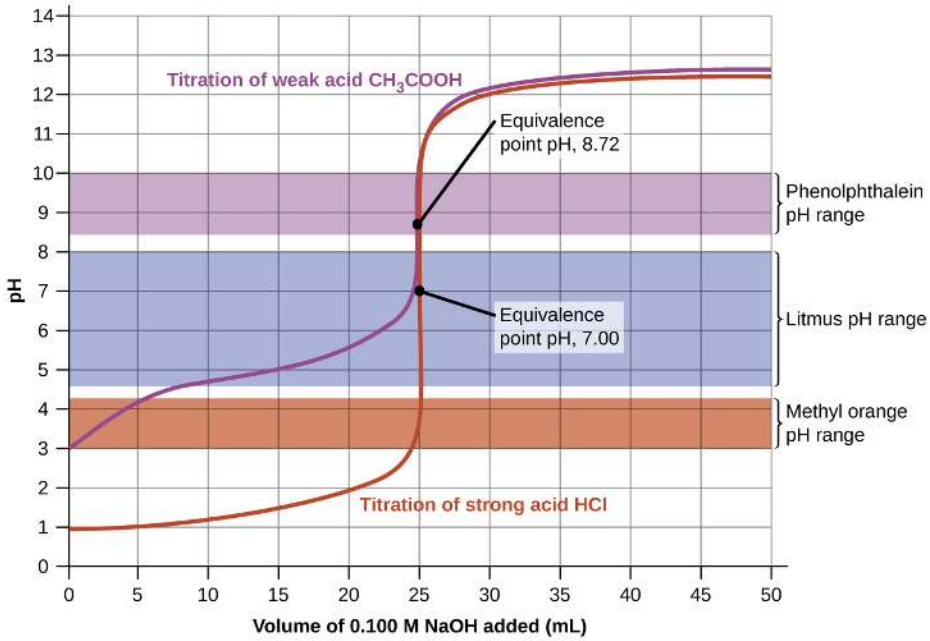


Figure 7.8.3: Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The weak acid titration curve in Figure 7.8.3 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 7.8: Acid-Base Titrations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **14.7: Acid-Base Titrations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.9: 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

---

This page titled 7.9: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

7.10: 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

$K_a K_b = 1.0 \times 10^{-14} = K_w$

$pK_a = -\log K_a$
$pK_b = -\log K_b$

This page titled 7.10: Key Equations is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

7.11: 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.

This page titled 7.11: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

7.12: Exercises

1.

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

2.

Write equations that show $H_2PO_4^-$ acting both as an acid and as a base.

3.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) H_3O^+

(b) HCl

(c) NH_3

(d) CH_3CO_2H

(e) NH_4^+

(f) HSO_4^-

4.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3

(b) PH_4^+

(c) H_2S

(d) CH_3CH_2COOH

(e) $H_2PO_4^-$

(f) HS^-

5.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) H_2O

(b) OH^-

(c) NH_3

(d) CN^-

(e) S^{2-}

(f) $H_2PO_4^-$

6.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) HS^-

(b) PO_4^{3-}

(c) NH_2^-

(d) C_2H_5OH

(e) O^{2-}

(f) $H_2PO_4^-$

7.

What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) OH^-

(b) H_2O

(c) HCO_3^-

(d) NH_3

(e) HSO_4^-

(f) H_2O_2

(g) HS^-

(h) $H_5N_2^+$

8.

What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) H_2S

(b) $H_2PO_4^-$

(c) PH_3

(d) HS^-

(e) HSO_3^-

(f) $H_3O_2^+$

(g) H_4N_2

(h) CH_3OH

9.

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

(b) $CN^- + H_2O \longrightarrow HCN + OH^-$

(c) $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$

(d) $HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O$

(e) $O^{2-} + H_2O \longrightarrow 2OH^-$

(f) $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $H_2S + NH_2^- \longrightarrow HS^- + NH_3$

10.

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$

(b) $HBr + H_2O \longrightarrow H_3O^+ + Br^-$

(c) $HS^- + H_2O \longrightarrow H_2S + OH^-$

(d) $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$

(e) $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$

(f) $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

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) $H_2PO_4^-$

(c) S^{2-}

(d) CO_3^{2-}

(e) HSO_4^-

13.

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

(a) NH_3

(b) HPO_4^-

(c) Br^-

(d) NH_4^+

(e) ASO_4^{3-}

14.

Is the self-ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.

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 2.9×10^{-14} at 40 °C.

16.

The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

17.

The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

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 1.7×10^{-6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?

25.

The hydroxide ion concentration in household ammonia is 3.2×10^{-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 $CH_3NH_3^+$, 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 $(CH_3)_2NH_2^+$, 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, $(CH_3)_2NH_2^+$ or $CH_3NH_3^+$, is the stronger acid?

38.

Which is the stronger acid, NH_4^+ or HBrO?

39.

Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$?

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) HSO_3^- or HSO_4^-

(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) HSO_4^- or $HSeO_4^-$

(b) NH_3 or H_2O

(c) PH_3 or HI

(d) NH_3 or PH_3

(e) H_2S or HBr

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) acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$

(b) basicity: BrO_2^-, ClO_2^-, IO_2^-

(c) acidity: HOCl, HOBr, HOI

(d) acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$

(e) basicity: NH_2^-, HS^-, HTe^-, PH_2^-

(f) basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-

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 NO_2^-, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

(a) HCl

(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

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: $[H_3O^+] = 1.34 \times 10^{-3}\ M$;
$[CH_3CO_2^-] = 1.34 \times 10^{-3}\ M$;

$[CH_3CO_2H] = 9.866 \times 10^{-2}\ M$;

(b) ClO^-: $[OH^-] = 4.0 \times 10^{-4}\ M$;

$[HClO] = 2.38 \times 10^{-4}\ M$;

$[ClO^-] = 0.273\ M$;

(c) HCO_2H: $[HCO_2H] = 0.524\ M$;
$[H_3O^+] = 9.8 \times 10^{-3}\ M$;
$[HCO_2^-] = 9.8 \times 10^{-3}\ M$;

(d) $C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233\ M$;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}\ M$;
$[H_3O^+] = 2.3 \times 10^{-3}\ M$

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: $[OH^-] = 3.1 \times 10^{-3}\ M$;
$[NH_4^+] = 3.1 \times 10^{-3}\ M$;

$[NH_3] = 0.533\ M$;

(b) HNO_2: $[H_3O^+] = 0.011\ M$;
$[NO_2^-] = 0.0438\ M$;

$[HNO_2] = 1.07\ M$;

(c) $(CH_3)_3N$: $[(CH_3)_3N] = 0.25\ M$;
$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}\ M$;

$[OH^-] = 3.7 \times 10^{-3}\ M$;

(d) NH_4^+ : $[NH_4^+] = 0.100\ M$;

$[NH_3] = 7.5 \times 10^{-6}\ M$;
$[H_3O^+] = 7.5 \times 10^{-6}\ M$

55.

Determine K_b for the nitrite ion, NO_2^-. In a 0.10-*M* solution this base is 0.0015% ionized.

56.

Determine K_a for hydrogen sulfate ion, HSO_4^-. 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^-

(b) NH_4^+

(c) AsO_4^{3-}

(d) $(CH_3)_2NH_2^+$

(e) NO_2^-

(f) $HC_2O_4^-$ (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) HTe^- (as a base)

(b) $(CH_3)_3NH^+$

(c) $HAsO_4^{2-}$ (as a base)

(d) HO_2^- (as a base)

(e) $C_6H_5NH_3^+$

(f) HSO_3^- (as a base)

59.

Using the K_a value of 1.4 Unexpected text node: 'Figure 14.7.'

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* $Fe(H_2O)_6^{2+}$ 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 HSO_4^- is 1.43. Determine K_a for HSO_4^- 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:
$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$

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: $[H_3O^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$? 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, $C_6H_4(CO_2H)_2$.

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \qquad K_a = 1.1 \times 10^{-3}$$
$$C_6H_4(CO_2H)(CO_2)(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2{}^{2-}(aq) \qquad K_a = 3.9 \times 10^{-6}$$

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 4.2×10^{-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* $NaCH_3CO_2$?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

81.

What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2{}^-(aq) \qquad K_a = 4.5 \times 10^{-5}$$

82.

What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3{}^+(aq) + OH^-(aq) \qquad K_b = 4.4 \times 10^{-4}$$

83.

What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

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 1.80×10^{-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 1.1×10^{-4}. In a 1.0×10^{-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 7.12: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

8: 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.

8.1: Introduction
8.2: Chemical Reaction Rates
8.3: Factors Affecting Reaction Rates
8.4: Rate Laws
8.5: Integrated Rate Laws
8.6: Collision Theory
8.7: Reaction Mechanisms
8.8: Catalysis
8.9: Key Terms
8.10: Key Equations
8.11: Summary
8.12: Exercises

This page titled 8: Kinetics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

8.1: 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 8.1.1: 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 8.1: Introduction is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

8.2: 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:

$$\begin{aligned} H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ \text{rate of decomposition of} \qquad &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta\,[H_2O_2]}{\Delta t} \end{aligned}$$

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\mathrm{H_2O_2}]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[\mathrm{H_2O_2}]_{t_2}$ 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, $\Delta\,[\mathrm{H_2O_2}]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. Figure 8.2.1 provides an example of data collected during the decomposition of $\mathrm{H_2O_2}$.

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 8.2.1: 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:

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

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:

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

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 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 8.2.2). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

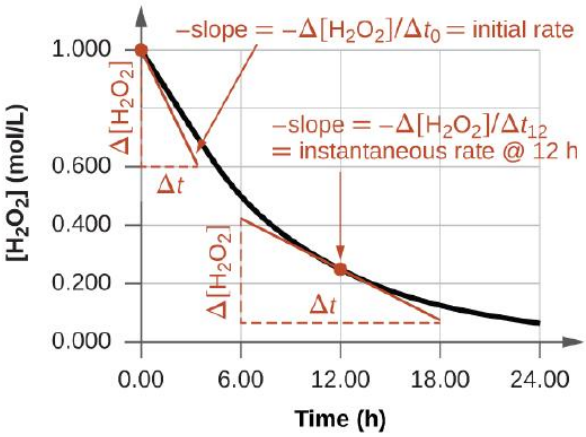


Figure 8.2.2: This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at 12 h).

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 8.2.3). 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.

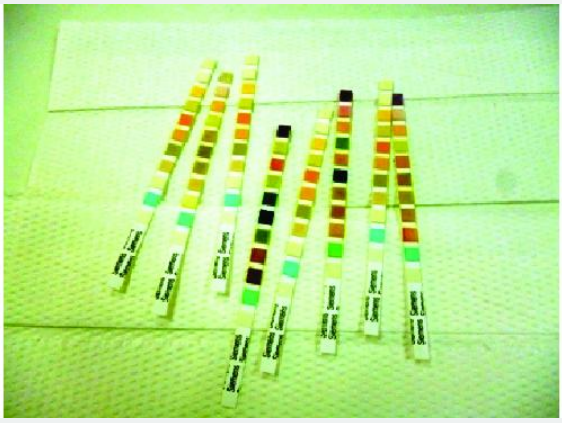


Figure 8.2.3: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

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

$$A \longrightarrow B \tag{8.2.1}$$

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:

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

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.

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

Figure 8.2.4: 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:

$$\frac{2.91\times10^{-6}M/s}{9.70\times10^{-7}M/s}\approx3$$

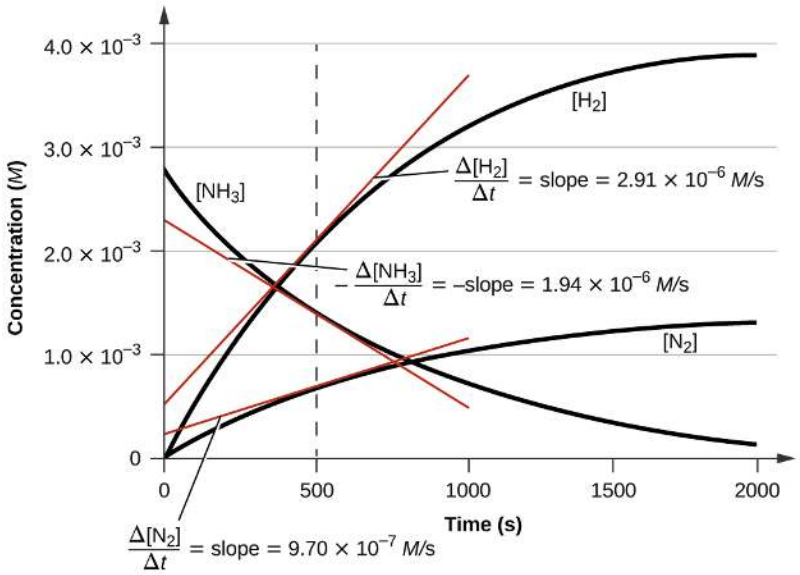


Figure 8.2.4: Changes in concentrations of the reactant and products for the reaction $2\,\mathrm{NH_3}\longrightarrow\mathrm{N_2}+3\,\mathrm{H_2}$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

Example 8.2.1: Expressions for Relative Reaction Rates

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

$$4NH_3(g)+5O_2(g)\longrightarrow4NO(g)+6H_2O(g) \tag{8.2.2}$$

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:

$$-\frac{1}{4}\frac{\Delta\left[NH_3\right]}{\Delta t}=-\frac{1}{5}\frac{\Delta\left[O_2\right]}{\Delta t}=\frac{1}{4}\frac{\Delta[NO]}{\Delta t}=\frac{1}{6}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Exercise 8.2.1

The rate of formation of Br_2 is 6.0 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

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

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

Answer

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

Example 8.2.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 8.2.2: 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:

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{8.2.3}$$

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

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{8.2.4}$$

Therefore:

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

and

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

Exercise 8.2.2

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 8.2: Chemical Reaction Rates is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

8.3: 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 8.3.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure 8.3.1: (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 8.3.2). 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 8.3.2: 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 8.3: Factors Affecting Reaction Rates is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

8.4: 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:

$$\text{rate } = k\left[H_2O_2\right]$$

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

$$\text{rate } = k\left[\mathrm{C_4H_6}\right]^2$$

describes a reaction that is second order in $\mathrm{C_4H_6}$ and second order overall. The rate law:

$$\text{rate } = k\left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right]$$

describes a reaction that is first order in $\mathrm{H^+}$, first order in $\mathrm{OH^-}$, and second order overall.

Example 8.4.1: Writing Rate Laws from Reaction Orders

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

$$\mathrm{NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)}$$

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

Solution

The reaction will have the form:

$$\text{rate } = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n$$

The reaction is second order in $\mathrm{NO_2}$; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate } = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[\text{CO}]^0 = 1$, 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 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 8.4.1A

The rate law for the reaction:

$$\text{H}_2(\text{g}) + 2\,\text{NO}(\text{g}) \longrightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$$

has been determined to be rate = $k[\text{NO}]^2[\text{H}_2]$. 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 H_2 = 1; overall order = 3

? Exercise 8.4.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($\text{CH}_3\text{CH}_2\text{OCOCH}_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{OCOCH}_3 \longrightarrow \text{CH}_3\text{OCOCH}_3 + \text{CH}_3\text{CH}_2\text{OH}$$

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

$$\text{rate } = k\left[\text{CH}_3\text{OH}\right]$$

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

Answer

order in CH_3OH = 1; order in $\text{CH}_3\text{CH}_2\text{OCOCH}_3$ = 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 8.4.2: 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 8.4.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

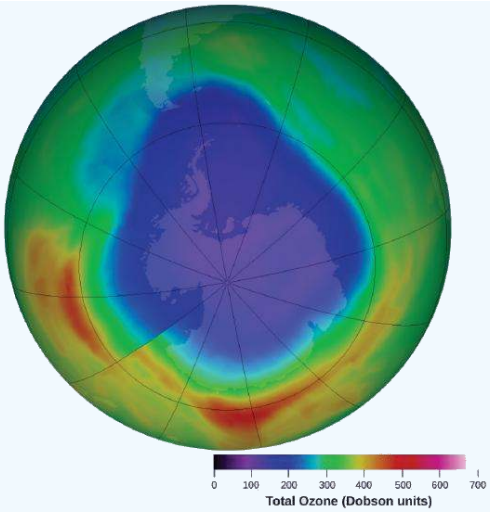


Figure 8.4.1: A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

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

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)	$\frac{\Delta[NO_2]}{\Delta t}(\mathrm{molL^{-1}s^{-1}})$
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:

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

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:

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

Step 3:

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

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

Exercise 8.4.2

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

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

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

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

Example 8.4.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

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

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 8.4.2, 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 8.4.3

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

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

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:

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

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

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

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:

$$\mathrm{NO_2 + CO \longrightarrow NO + CO_2} \qquad \text{rate } = k[NO_2]^2$$

$$\mathrm{CH_3CHO \longrightarrow CH_4 + CO} \qquad \text{rate } = k[CH_3CHO]^2$$

$$\mathrm{2\,N_2O_5 \longrightarrow NO_2 + O_2} \qquad \text{rate } = k\left[N_2O_5\right]$$

$$\mathrm{2\,NO_2 + F_2 \longrightarrow 2\,NO_2F} \qquad \text{rate } = k\left[NO_2\right]\left[F_2\right]$$

$$\mathrm{2\,NO_2Cl \longrightarrow 2\,NO_2 + Cl_2} \qquad \text{rate } = k\left[NO_2Cl\right]$$

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 8.4.2 was determined to be k was derived to be $\mathrm{L\,mol^{-1}s^{-1}}$. For the third-order reaction, k was derived to be $\mathrm{L^2mol^{-2}s^{-1}}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $\mathrm{L^{x-1}\ mol^{1-x}s^{-1}}$. Table 8.4.1 summarizes the rate constant units for common reaction orders.

Table 8.4.1: Rate Constant Units for Common Reaction Orders

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

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 8.4: Rate Laws is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

8.5: 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 8.5.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is 9.2 10^{-3} s^{-1}:

$$C_4H_8 \longrightarrow 2\,C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

Since 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 0.200*x*. 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 8.5.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. 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:

$$\begin{aligned} \ln[A]_t &= (-k)(t) + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

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 8.5.2: Graphical Determination of Reaction Order and Rate Constant

Show that the data in Figure 8.5.1 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 8.5.1 are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in Figure 8.5.1.

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

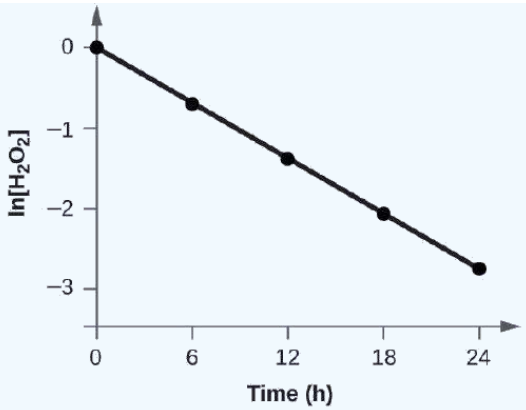


Figure 8.5.1: A linear relationship between $\ln[H_2O_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

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

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

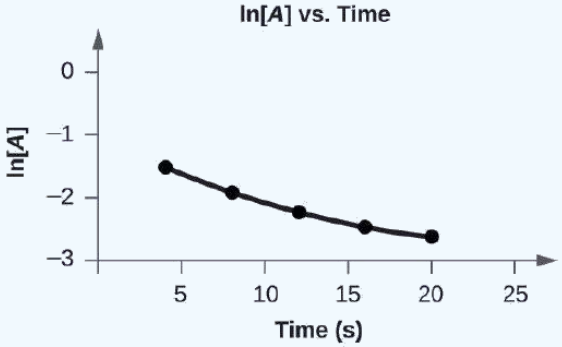
Exercise 8.5.2

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 8.5.3: 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 8.5.3

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 8.5.4: Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example 8.5.3. 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 8.5.2, 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.

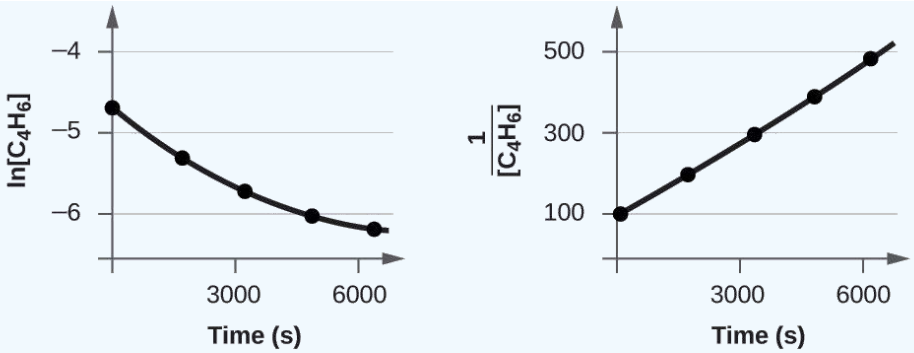


Figure 8.5.2: These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

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:

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

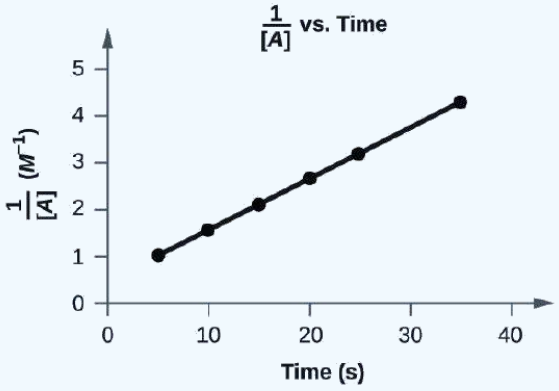
Exercise 8.5.4

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 8.5.3 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 8.5.5: Graphical Determination of Zero-Order Rate Constant

Use the data plot in Figure 8.5.3 to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

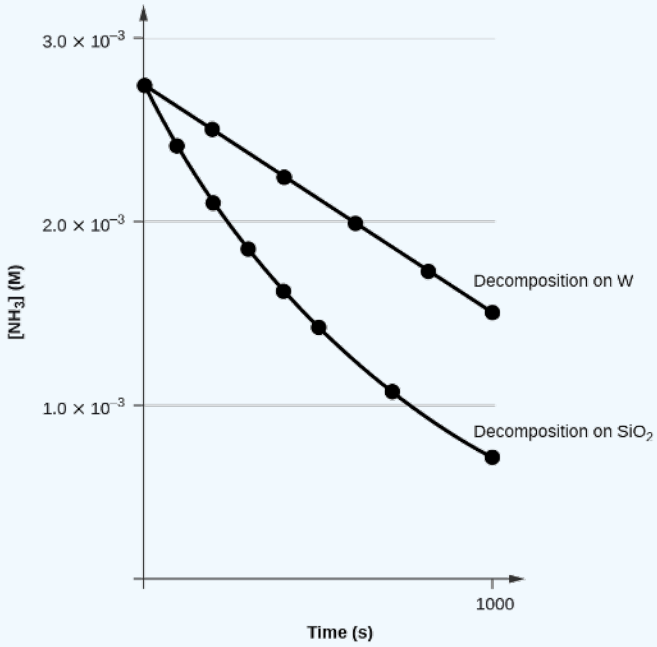


Figure 8.5.3: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

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:

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

Exercise 8.5.5

The zero-order plot in Figure 8.5.3 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 8.5.1) 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 8.5.6: 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 8.5.4.



Figure 8.5.4: 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 8.5.4 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 8.5.1

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:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

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

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

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:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

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

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

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 8.5.1.

Table 8.5.1: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of 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 8.5.7: Half-Life for Zero-Order and Second-Order Reactions

What is the half-life for the butadiene dimerization reaction described in Example 8.5.3?

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 8.5.7

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see Figure 8.5.3)?

Answer

87 min

This page titled 8.5: Integrated Rate Laws is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

8.6: 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 8.6.1. 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.

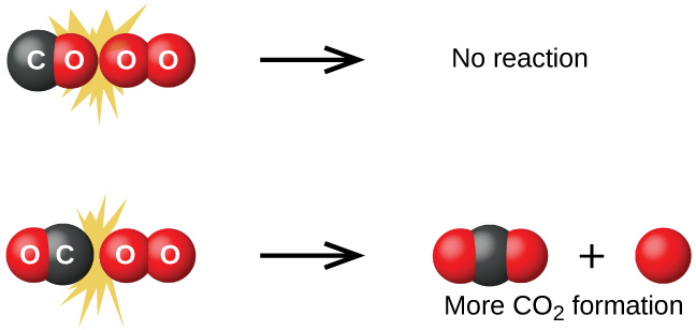


Figure 8.6.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

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 8.6.2 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.

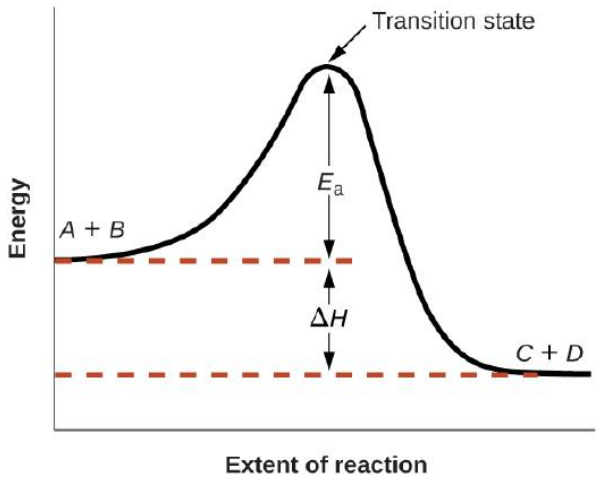


Figure 8.6.2: Reaction diagram for the exothermic reaction

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 8.6.3*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 8.6.3*b*. This yields a greater value for the rate constant and a correspondingly faster reaction rate.

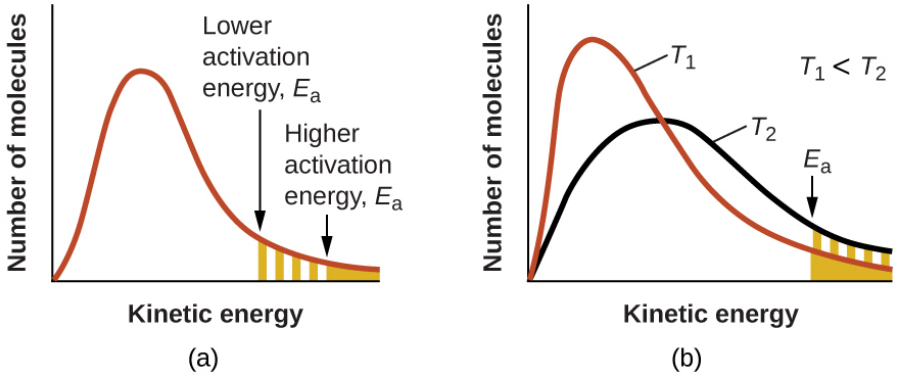


Figure 8.6.3: Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

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 8.6.1: Determination of E_a

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

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

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 8.6.4 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.

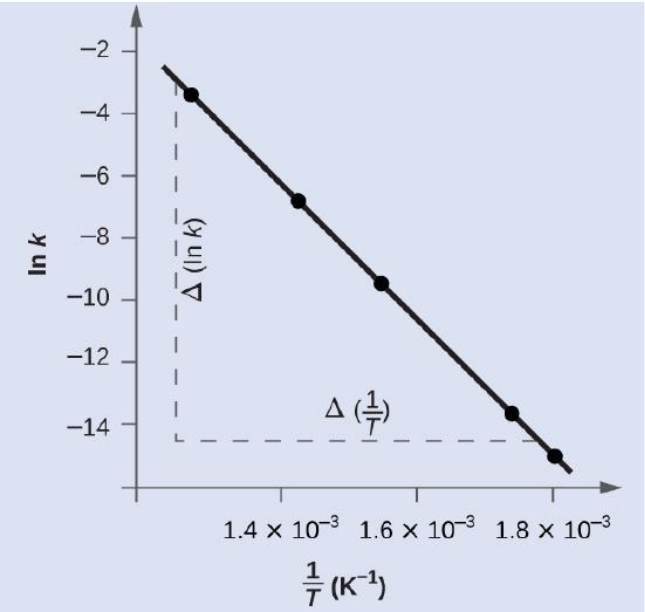


Figure 8.6.4: This graph shows the linear relationship between $\ln k$ versus $\frac{1}{T}$ for the reaction $2HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

$$\begin{aligned}\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.860)-(-3.231)}{\left(1.80\times10^{-3}K^{-1}\right)-\left(1.28\times10^{-3}K^{-1}\right)} \\ &= \frac{-11.629}{0.52\times10^{-3}K^{-1}} = -2.2\times10^{4}K \\ &= -\frac{E_a}{R} \\ E_a &= -\text{ slope }\times R = -\left(-2.2\times10^{4}K\times8.314Jmol^{-1}K^{-1}\right) \\ &\quad 1.8\times10^{5}Jmol^{-1} \text{ or } 180kJmol^{-1}\end{aligned}$$

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:

$$E_a = -8.314Jmol^{-1}K^{-1}\left(\frac{-3.231-(-14.860)}{1.28\times10^{-3}K^{-1}-1.80\times10^{-3}K^{-1}}\right)$$

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 8.6.1

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

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

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 8.6: Collision Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

8.7: 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:

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

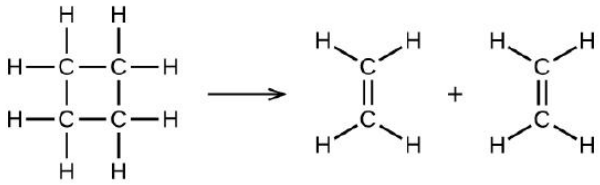
The rate law for a unimolecular reaction is first order:

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

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:

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

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 8.7.1)



Figure 8.7.1: 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 8.7.2.



Figure 8.7.2: 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 8.7.1: 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:

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

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 8.7.1

The first step of a proposed multistep mechanism is:

$$\boxed{\ce{F2(g) <=> 2 F(g) \tag{fast}}}$$

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 8.7: Reaction Mechanisms is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

8.8: 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

Catalysts Do Not Affect Equilibrium

A catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

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

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year.

Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Portrait of a Chemist

Fritz Haber

In the early 20th century, German chemist Fritz Haber (Figure 17.19) developed a practical process for converting diatomic nitrogen, which cannot be used by plants as a nutrient, to ammonia, a form of nitrogen that is easiest for plants to absorb.

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

The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen ($\mathrm{N_2}$) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate. Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008.



Figure 8.8.1The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive

devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

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

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H = -92.2\ \text{kJ}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure 17.20).

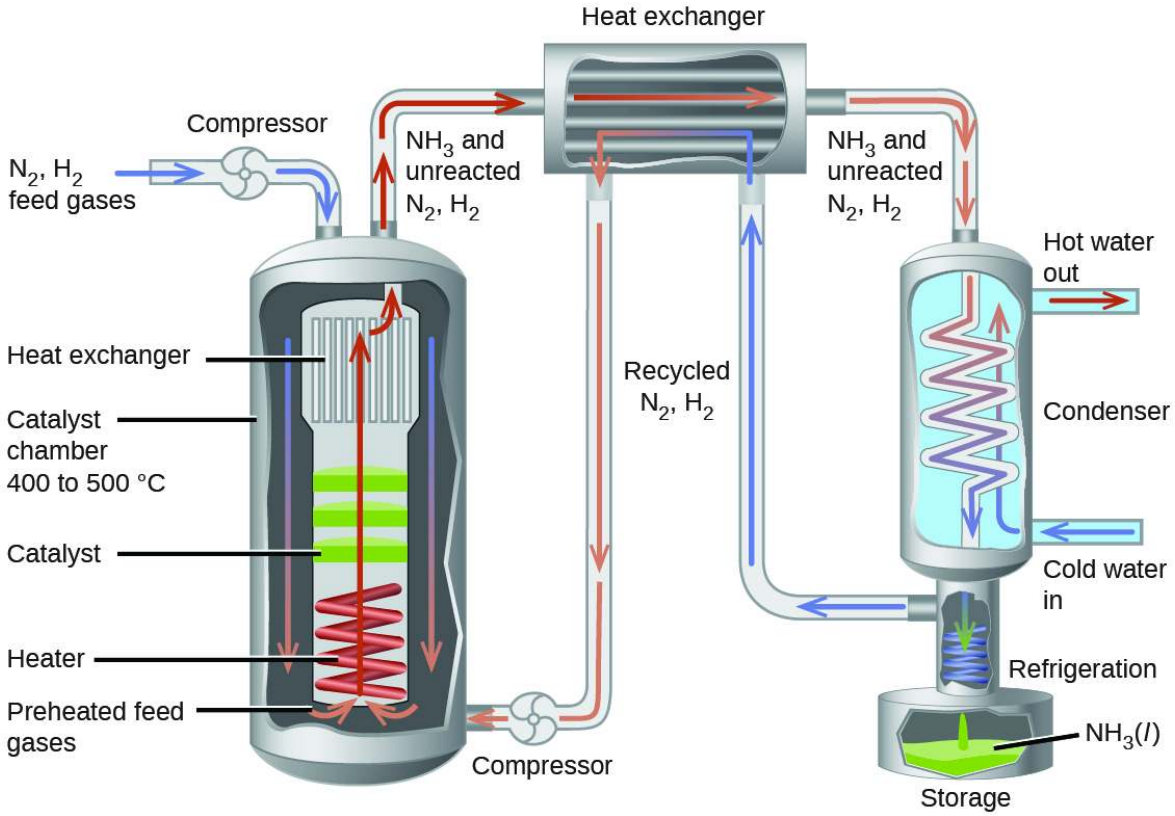


Figure 8.8.2Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

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 8.8.3shows 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).

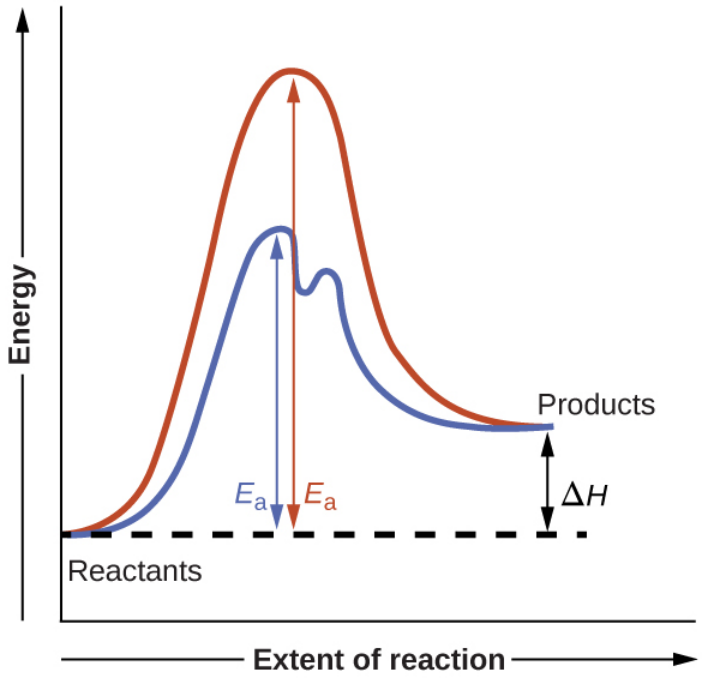
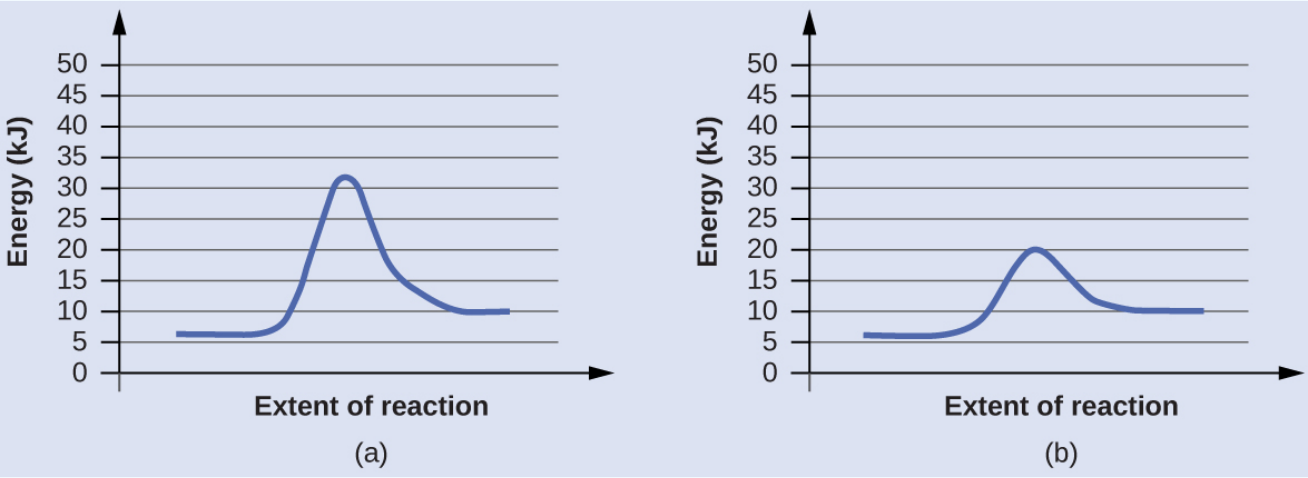


Figure 8.8.4Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 17.15

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.

$$\text{diagram (a): } E_\text{a} = 32\ \text{kJ} - 6\ \text{kJ} =$$

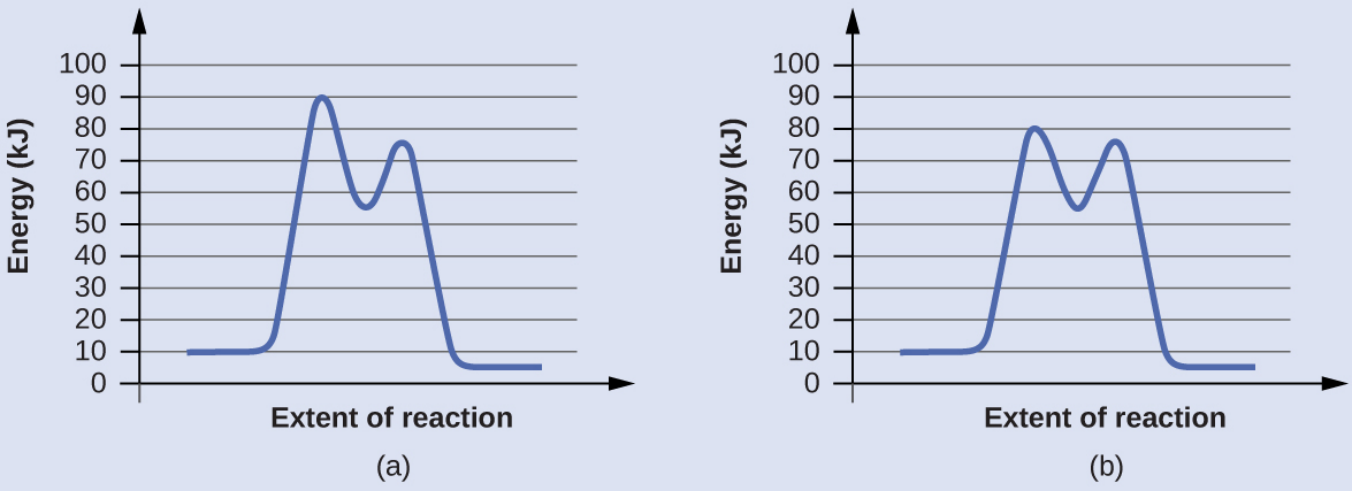
$$\text{diagram (b): } E_\text{a} = 20\ \text{kJ} - 6\ \text{kJ} =$$

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

Check Your Learning

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:

$$3O_2(g) \rightarrow h\nu \;\; 2O_3(g)$$

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:

$$\begin{aligned}&\mathrm{O_3} \longrightarrow \mathrm{O_2 + O}\\&\mathrm{O+}\end{aligned}$$

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:

$$\begin{aligned}&\mathrm{NO}(g) + \mathrm{O_3}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g)\\&\mathrm{O_3}(g) \longrightarrow \mathrm{O_2}(g) + \mathrm{O}(g)\\&\mathrm{NO_2}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{O_2}(g)\end{aligned}$$

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

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

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 17.22), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[2] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).

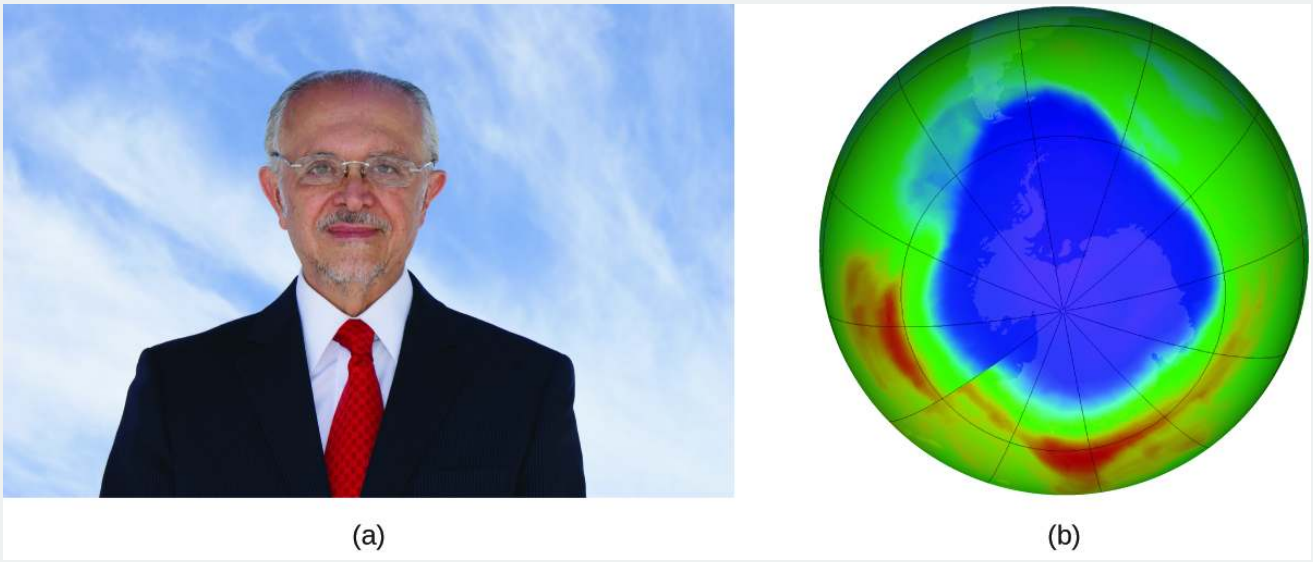


Figure 8.8.5(a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

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:

$$\mathrm{CH_3Cl + OH \longrightarrow Cl + other}$$

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

$$\mathrm{Cl} + \mathrm{O_3} \longrightarrow \mathrm{ClO} +$$
$$\mathrm{O_2}$$
$$\mathrm{ClO}$$
$$+\mathrm{O} \longrightarrow \mathrm{Cl} +$$
$$\mathrm{O_2}$$
$$\text{overall}$$
$$\text{Reaction: } \mathrm{O_3} +$$

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 $ClONO_2$.

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

How Sciences Interconnect

Glucose-6-Phosphate Dehydrogenase Deficiency

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 17.23, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure 17.24).

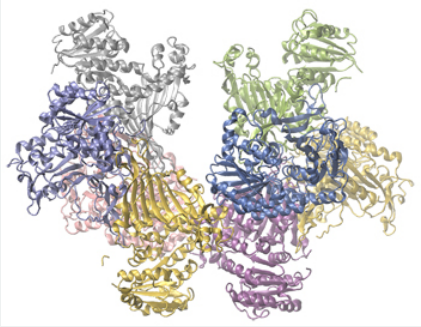


Figure 8.8.6Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

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.

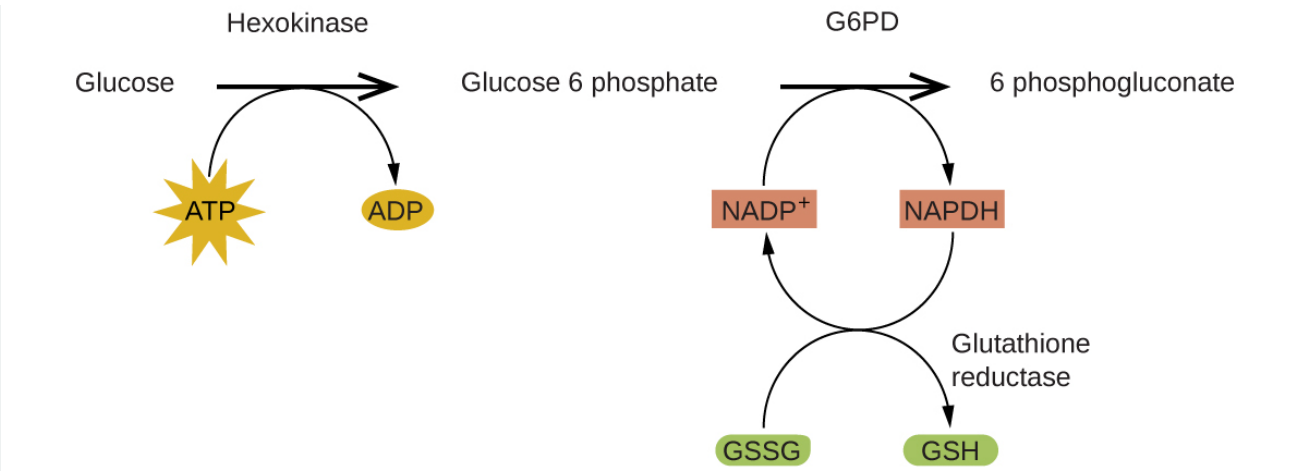


Figure 17.24 In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

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)
4. Desorption of product(s) from the surface of the catalyst

Figure 8.8.7 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).

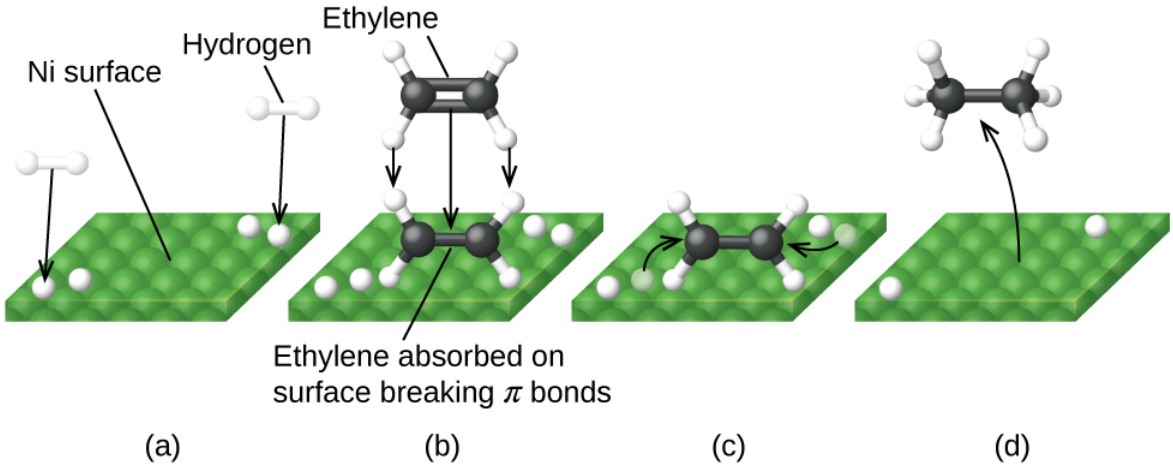


Figure 8.8.8Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C-C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface 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 17.26).

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 17.26).

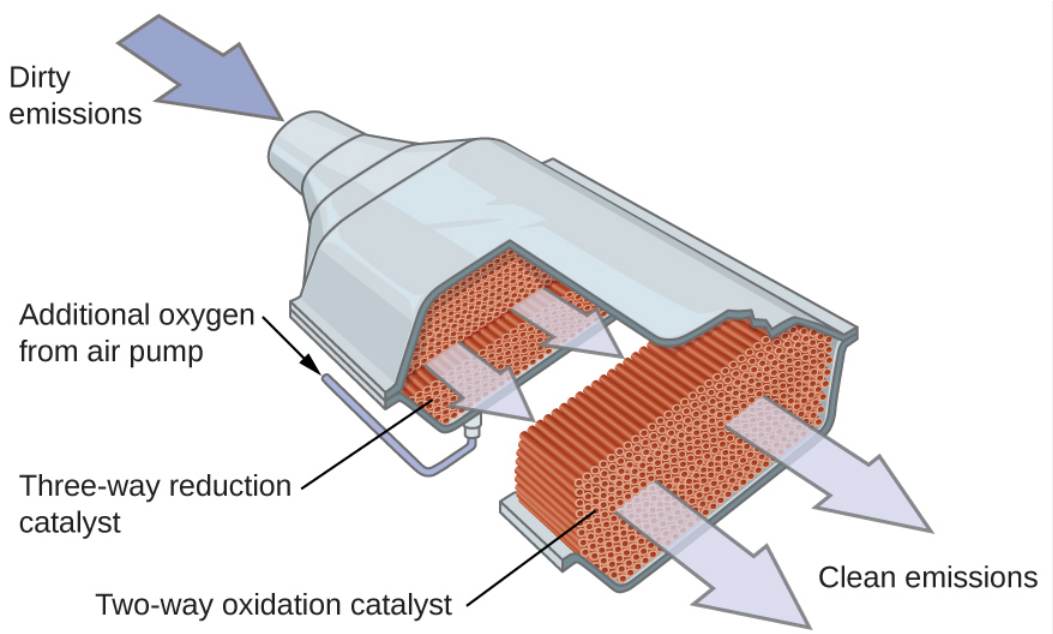


Figure 8.8.9A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

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 University of California at Davis' "ChemWiki" 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 17.3.

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

Table 8.8.1

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 17.27).

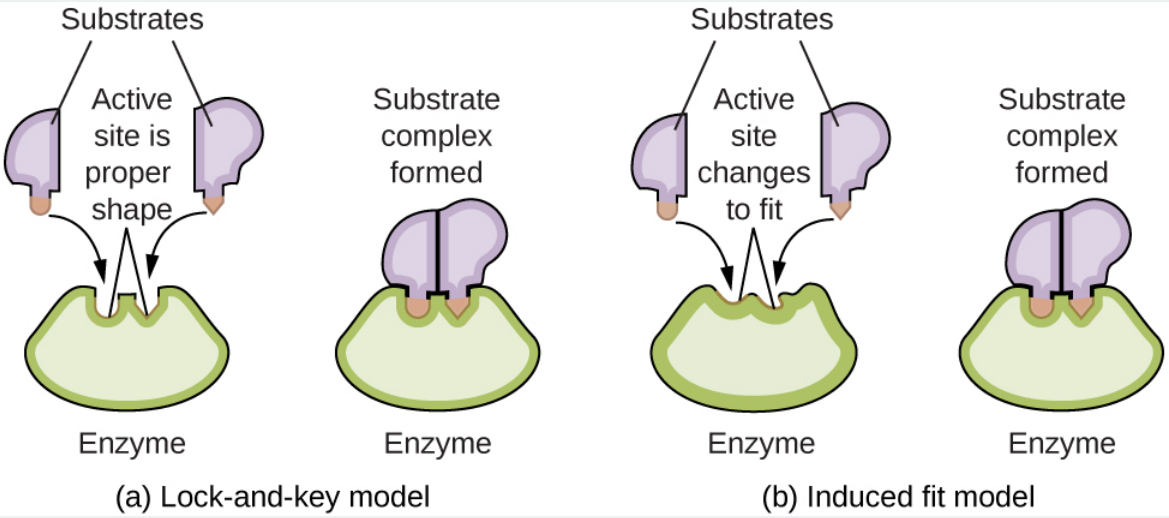


Figure 8.8.1 (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

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

The connection between the rate of a reaction and its equilibrium constant is one we can easily determine with just a bit of algebraic substitution. For a reaction where substance A forms B (and the reverse)

$$A \rightleftharpoons B$$

The rate of the forward reaction is

$$\text{Rate}(f) = k(f)[A]$$

And the rate of the reverse reaction is

$$\text{Rate}(r) = k(r)[B]$$

Once equilibrium is established, the rates of the forward and reverse reactions are equal:

$$\text{Rate}(f) = \text{Rate}(r) = k(f)[A] = k(r)[B]$$

Rearranging a bit, we get

$$\text{Rate}_f = \text{Rate}_r \text{ so } k(f)[A] = k(r)[B]$$

Also recall that the equilibrium constant is simply the ratio of product to reactant concentration at equilibrium:

$$\frac{k(f)}{k(r)} = \frac{[B]}{[A]}$$

$$K = \frac{[B]}{[A]}$$

So the equilibrium constant turns out to be the ratio of the forward to the reverse rate constants. This relationship also helps cement our understanding of the nature of a catalyst. That is, a catalyst does not change the fundamental equilibrium (or the underlying thermodynamics) of a reaction. Rather, what it does is alter the rate constant for the reaction – that is, both rate constants, forward and reverse, equally. In doing so, catalysts usually speed up the rate at which reactions attain equilibrium (though they can be used to slow down the rate of reaction as well!).

Footnotes

- 1Herrlich, P. "The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?" *EMBO Reports* 14 (2013): 759–764.
- 2"The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

This page titled 8.8: Catalysis is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

8.9: 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

---

This page titled 8.9: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

8.10: 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

This page titled 8.10: Key Equations is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

8.11: 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).

This page titled 8.11: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

8.12: Exercises

1.

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

2.

Ozone decomposes to oxygen according to the equation $2O_3(g) \longrightarrow 3O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

3.

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

4.

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:
$2C_4H_6 \longrightarrow C_8H_{12}$

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

(a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.

(b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?

(c) Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

5.

A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

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:
$5Br^-(aq) + BrO_3{}^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$

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: $CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$ if the rate law for the reaction is $\text{rate} = k[NO_2]^2$?

(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: $CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$ if the rate law for the reaction is $\text{rate} = k\,[NO_2]\,[CO]$?

(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 $NO + O_3 \longrightarrow NO_2 + O_2$ 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:

$^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-$

rate = $4.85 \times 10^{-2}\ \text{day}^{-1}\left[{}^{32}P\right]$

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):

$^{14}_{6}C \longrightarrow {}^{14}_{7}N + e^-$

$\text{rate} = k\left[{}^{14}_{6}C\right]$

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.

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

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 $A \longrightarrow 2C$.

[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:

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

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:

$$H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

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 $A \longrightarrow B + C$, 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 $Q \longrightarrow W + X$, 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}.

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

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) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(c) $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

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:

$I^- + OCl^- \longrightarrow IO^- + Cl^-$

	1	2	3
$[I^-]_{initial}$ (*M*)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (*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: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

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, $2O_3(g) \longrightarrow 3O_2(g)$. 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:
$2X \longrightarrow Y + Z$

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? $\left({}^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-\right)$ 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? $\left({}^{14}_{6}C \longrightarrow {}^{14}_{7}N + e^-\right)$ 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.

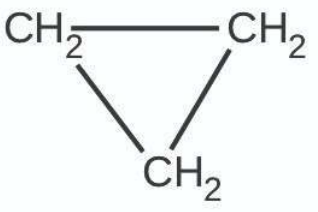
[Penicillin] (*M*)	Rate (mol L^{-1} min^{-1})
2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

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, $CH_3CH=CH_2$, 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 $^{18}_{9}\mathrm{F} \longrightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{+1}\mathrm{e}$) 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 $\frac{1}{64}$ 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.

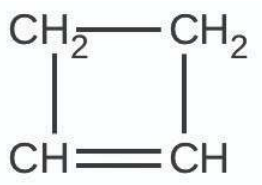
48.

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 $(CH_2=CH-CH=CH_2)$ has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as $2.0 \times 10^{-4}\ s^{-1}$ 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 $C_4H_8 \longrightarrow 2C_2H_4$ is $6.1 \times 10^{-8}\ s^{-1}$, 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,
$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

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, $k = 2.1 \times 10^{-11}$ 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 $A + BC \longrightarrow AB + C$ 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 $A + BC \longrightarrow AB + C$ 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 $A + B \longrightarrow C$? 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 $A + 2B \longrightarrow$ products? For $3A \longrightarrow$ products?

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?

(a) $\ce{Cl2 + CO -> Cl2CO}$
$\text{rate} = k[\ce{Cl2}]^{3/2}[\ce{CO}]$

(b) $\ce{PCl3 + Cl2 -> PCl5}$
$\text{rate} = k[\ce{PCl3}][\ce{Cl2}]$

(c) $\ce{2NO + H2 -> N2 + H2O2}$
$\text{rate} = k[\ce{NO}][\ce{H2}]$

(d) $\ce{2NO + O2 -> 2NO2}$
$\text{rate} = k[\ce{NO}]^2[\ce{O2}]$

(e) $\ce{NO + O3 -> NO2 + O2}$
$\text{rate} = k[\ce{NO}][\ce{O3}]$

72.

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

(a) $\ce{O3 ->[sunlight] O2 + O}$

(b) $\ce{O3 + Cl -> O2 + ClO}$

(c) $\ce{ClO + O -> Cl + O2}$

(d) $\ce{O3 + NO -> NO2 + O2}$

(e) $\ce{NO2 + O -> NO + O2}$

73.

Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:
$\ce{2NO + 2H2 -> N2 + 2H2O}$

What would the rate law be if the mechanism for this reaction were:
$2NO + H_2 \longrightarrow N_2 + H_2O_2$ (slow)
$H_2O_2 + H_2 \longrightarrow 2H_2O$ (fast)

74.

Experiments were conducted to study the rate of the reaction represented by this equation.[3]
$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

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) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.

(b) Write the overall rate law for the reaction.

(c) Calculate the value of the rate constant, *k*, for the reaction. Include units.

(d) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.

(e) The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

Step 2: $N_2O_2 + H_2 \rightleftharpoons H_2O + N_2O$

Step 3: $N_2O + H_2 \rightleftharpoons N_2 + H_2O$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

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:
$Cl_2(g) \rightleftharpoons 2Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
$CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)
$COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (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:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$
$$O_3 + Cl \longrightarrow O_2 + ClO$$
$$ClO + O \longrightarrow Cl + O_2$$

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:
$2O_3 \longrightarrow 3O_2$

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

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$
$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

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

79.

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction: $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

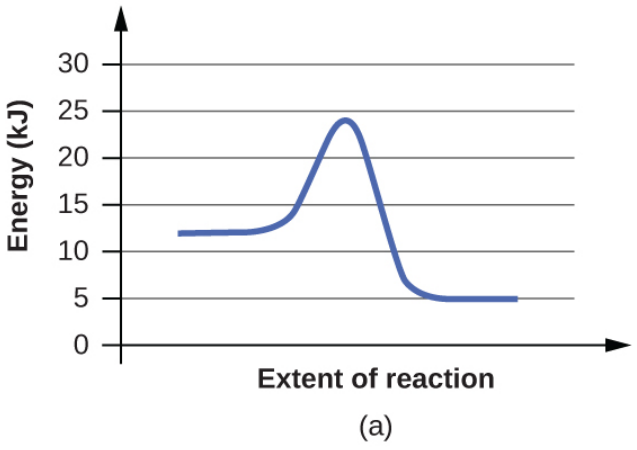
80.

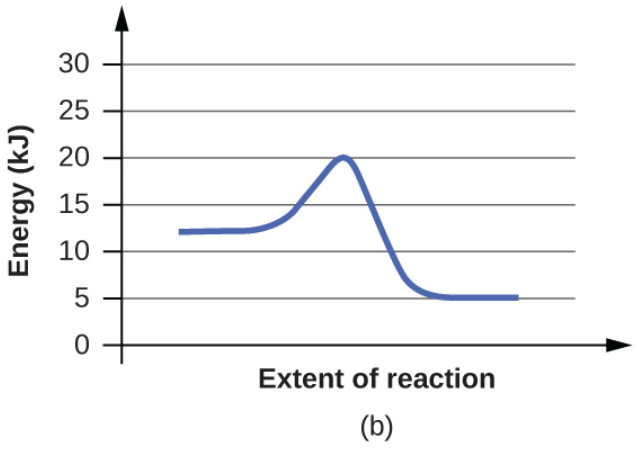
Nitrogen and oxygen react at high temperatures. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

81.

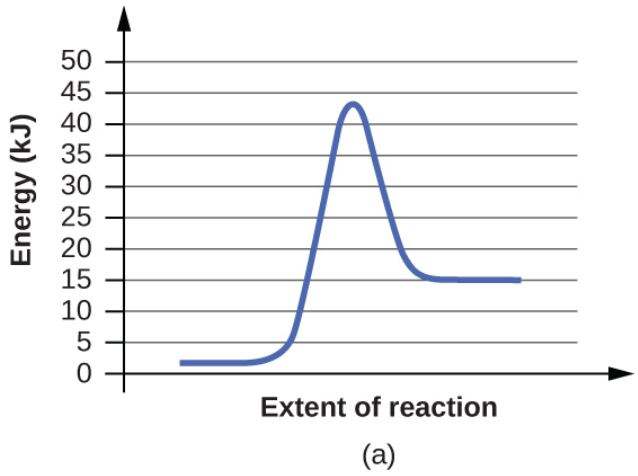
For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

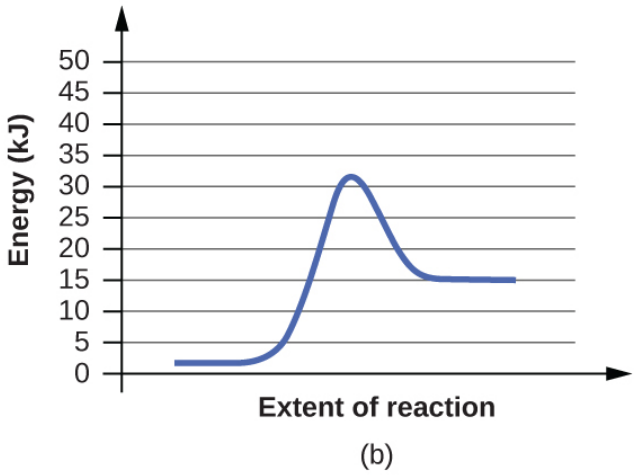
(a)





(b)

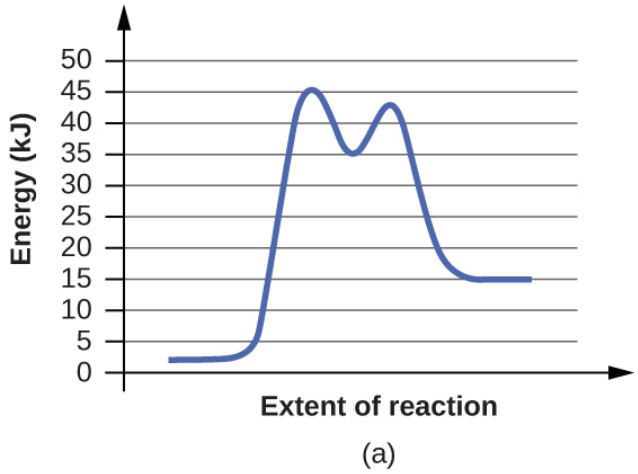


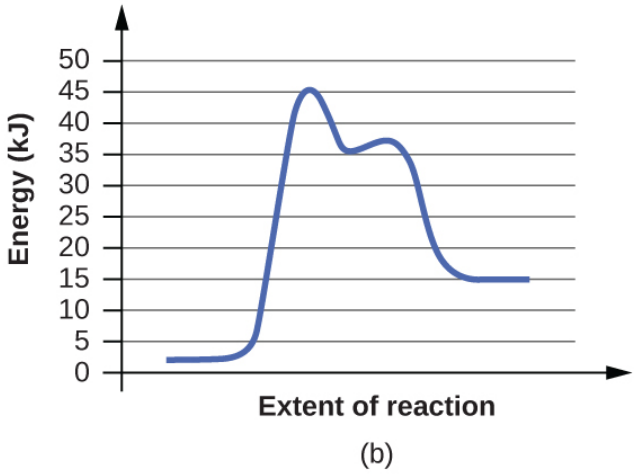


82.

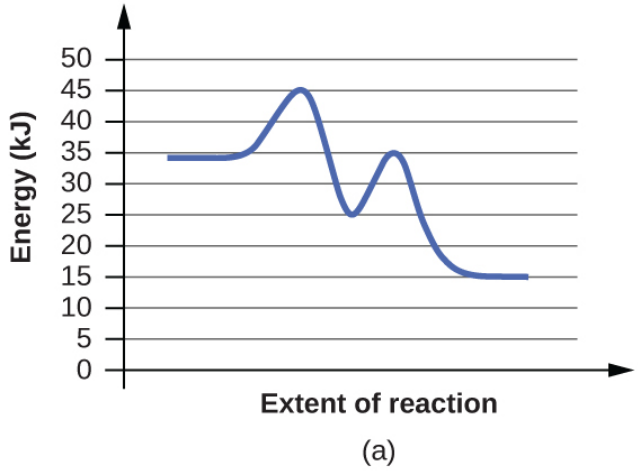
For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

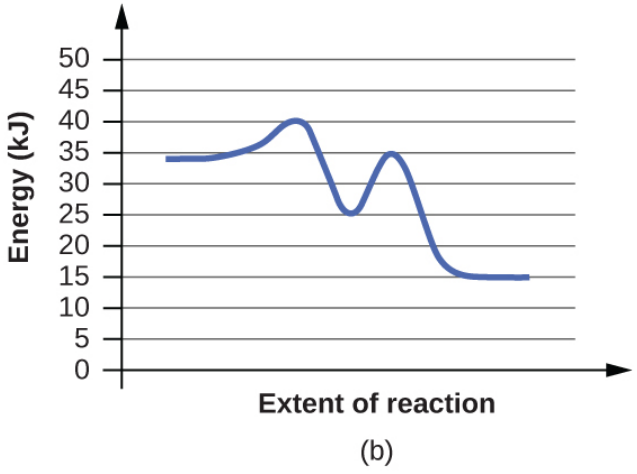
(a)





(b)

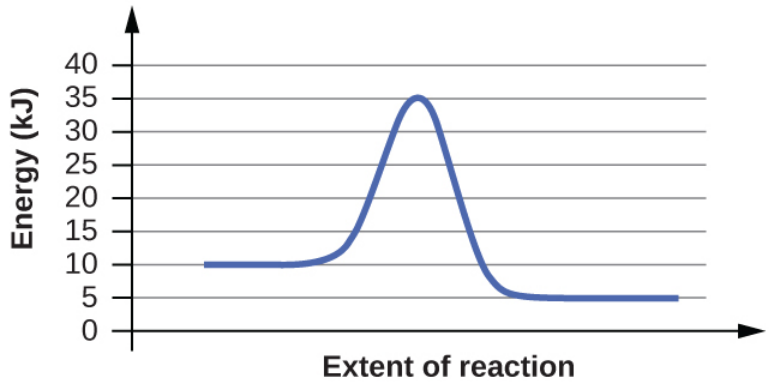




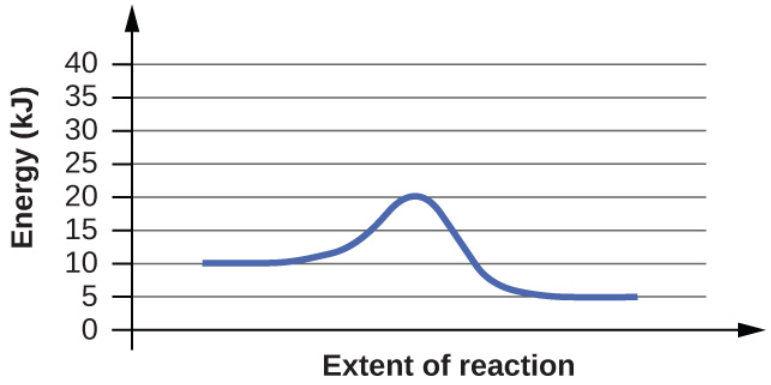
83.

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

(a)



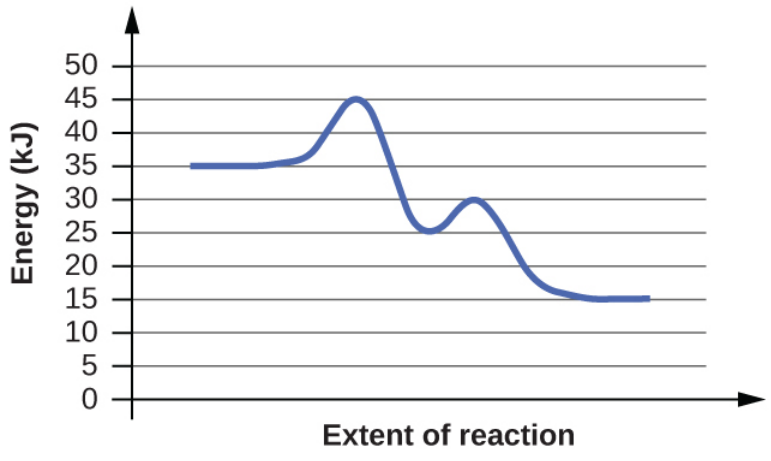
(b)



84.

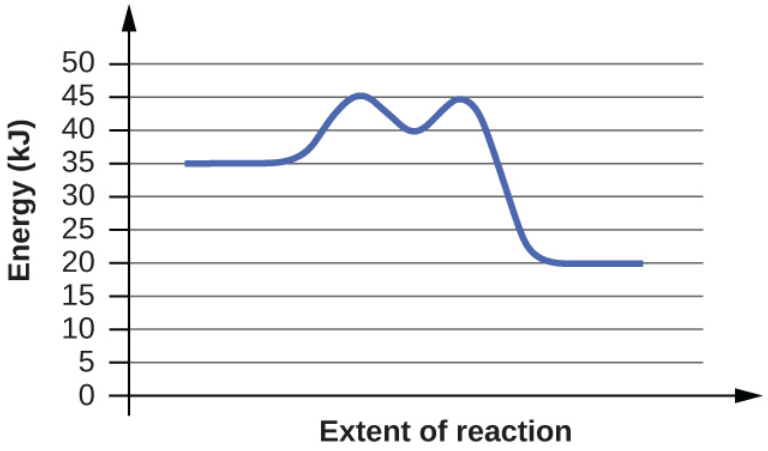
For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)

https://chem.libretexts.org/@go/page/456103



85.

Assuming the diagrams in Exercise 17.83 represent different mechanisms for the same reaction, which of the reactions has the faster rate?

86.

Consider the similarities and differences in the two reaction diagrams shown in Exercise 17.84. 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

- 3This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

This page titled 8.12: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

9: 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.

9.1: Introduction
9.2: Review of Redox Chemistry
9.3: Galvanic Cells
9.4: Electrode and Cell Potentials
9.5: Potential, Free Energy, and Equilibrium
9.6: Batteries and Fuel Cells
9.7: Corrosion
9.8: Electrolysis
9.9: Key Terms
9.10: Key Equations
9.11: Summary
9.12: Exercises

This page titled 9: Electrochemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

9.1: 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 9.1.1). In this chapter, the essential concepts of electrochemistry will be addressed.



Figure 9.1.1: Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

This page titled 9.1: Introduction is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

- **17.0: Introduction** is licensed CC BY 4.0.

9.2: 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, 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:

$$\mathrm{NaCl(l)}\longrightarrow\mathrm{Na(l)}+\mathrm{Cl_2(g)}\qquad\text{(unbalanced)}$$

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:

$$2\,\mathrm{NaCl(l)}\longrightarrow 2\,\mathrm{Na(l)}+\mathrm{Cl_2(g)}\qquad\text{(balanced)}$$

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 9.2.1: 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.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{HNO_3(aq) \longrightarrow NO(g)}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{HNO_3(aq) \longrightarrow NO(g)}$$

Step 3: Balance each half-reaction for O by adding H_2O.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{HNO_3(aq) \longrightarrow NO(g) + \mathbf{2\,H_2O(l)}}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{\mathbf{3\,H^+(aq)} + HNO_3(aq) \longrightarrow NO(g) + 2\,H_2O(l)}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq) + \mathbf{2\,e^-}}$$

$$\text{reduction:} \quad \mathrm{\mathbf{3\,e^-} + 3\,H^+(aq) + HNO_3(aq) \longrightarrow NO(g) + 2\,H_2O(l)}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

$$\text{oxidation } (\times 3): \quad \mathrm{\mathbf{3}\,Cu(s) \longrightarrow \mathbf{3}\,Cu^{2+}(aq) + \mathbf{6}\ \cancel{2}e^-}$$

$$\text{reduction } (\times 2): \quad \mathrm{\mathbf{6}\ \cancel{3}e^- + \mathbf{6}\ \cancel{3}H^+(aq) + \mathbf{2}\,HNO_3(aq) \longrightarrow \mathbf{2}\,NO(g) + \mathbf{4}\ \cancel{2}H_2O(l)}$$

Step 7: Add the two half-reactions and simplify.

$$3\,Cu(s) + \cancel{6\,e^-} + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + \cancel{6\,e^-} + 2\,NO(g) + 4\,H_2O(l)$$

$$3\,Cu(s) + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)$$

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 9.2.1

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 9.2.2: 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.

$$\text{oxidation:} \quad \mathbf{H_2O(l)} + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$$

$$\text{reduction:} \quad MnO_4^-(aq) \longrightarrow MnO_2(s) + \mathbf{2\,H_2O(l)}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\text{oxidation:} \quad H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + \mathbf{5\,H^+(aq)}$$

$$\text{reduction:} \quad \mathbf{4\,H^+(aq)} + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq) + \mathbf{3\,e^-}$$

$$\text{reduction:} \quad \mathbf{3\,e^-} + 4\,H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

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.

$$\cancel{H_2O(l)} + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + 5\cancel{1}\, H^+(aq) + \cancel{3e^-}$$

$$+ \quad \cancel{3e^-} + 4\, H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\cancel{1}\, H_2O(l)$$

$$Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H^+(aq) + H_2O(l)$$

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.

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + \cancel{H^+(aq)} + H_2O(l) + \cancel{OH^-(aq)}$$

after neutralizing the H^+, we get the balanced equation for the reaction in a basic solution

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2\, H_2O(l)$$

Exercise 9.2.2

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

$$H_2O(l) + 2\, MnO_4^-(aq) + Br^-(aq) \longrightarrow 2\, MnO_2(s) + BrO_3^-(aq) + 2\, OH^-(aq)$$

This page titled 9.2: Review of Redox Chemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **17.1: Review of Redox Chemistry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.3: 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 9.3.1: 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 9.3.1: 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 9.3.2. 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.

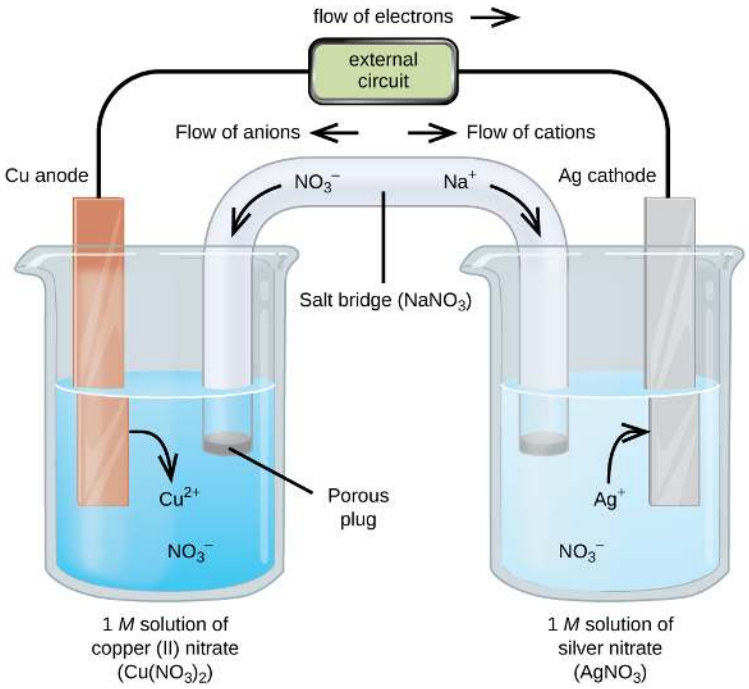


Figure 9.3.2: A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.

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 9.3.2: 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 9.3.3) 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.

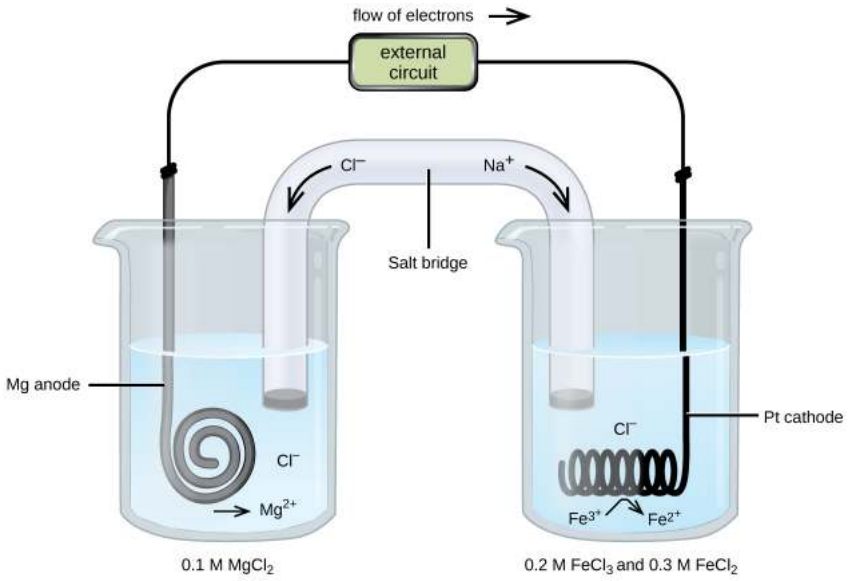


Figure 9.3.3: A galvanic cell based on the spontaneous reaction between magnesium and iron(III) ions.

Example 9.3.1: 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 9.3.1

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 9.3: Galvanic Cells is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

9.4: 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:

$$2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2(g)}$$

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 9.4.1).

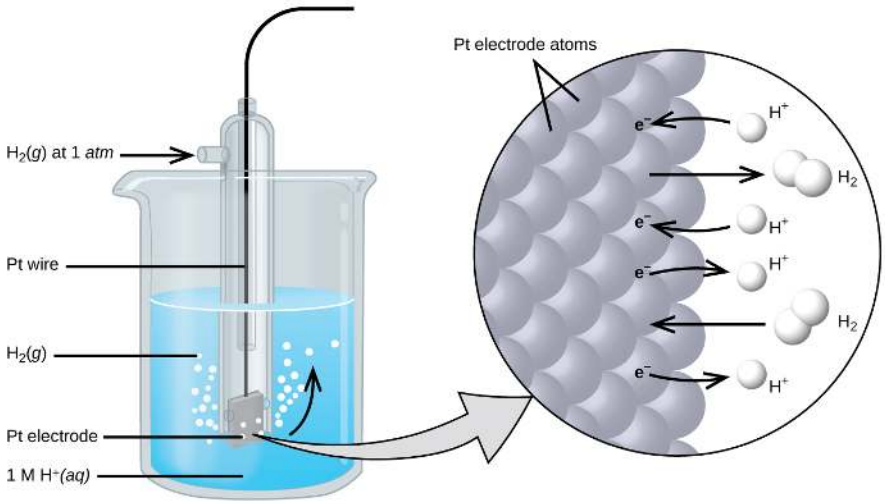


Figure 9.4.1: A standard hydrogen electrode (SHE).

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 9.4.2: , 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.

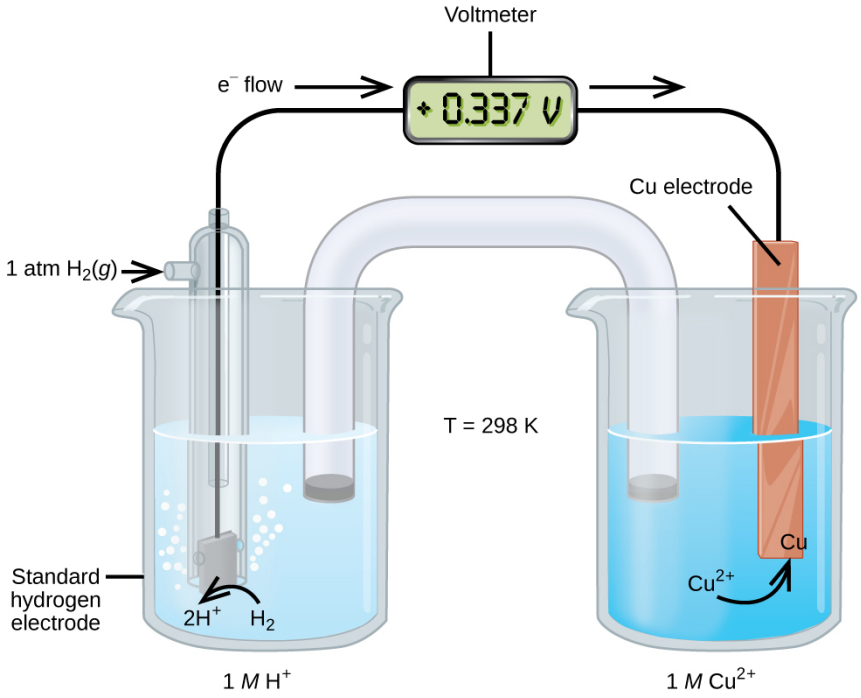


Figure 9.4.2: A cell permitting experimental measurement of the standard electrode potential for the half-reaction

Table 9.4.1 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 or in the following resource: (libretext list of reduction potentials)

Table 9.4.1: Selected Standard Reduction Potentials at 25 °C

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

Half-Reaction	$E°$ (V)
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+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
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-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 9.4.1: 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:

$$\begin{array}{lll} \text{anode:} & \mathrm{Cu(s) \longrightarrow Cu^{2+} + 2\,e^-} & \\ \text{cathode:} & \mathrm{2\,Ag^+(aq) + 2\,e^- \longrightarrow 2\,Ag(s)} & \\ \hline \text{cell:} & \mathrm{Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+} + 2\,Ag(s)} & E^o_{\text{cell}} = 0\,\text{V} \end{array}$$

The standard cell potential computed as

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{Ag} - E^\circ_{Cu} \\ &= 0.7996V - 0.34V \\ &= +0.46V \end{aligned}$$

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:

$$\mathrm{Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)}$$

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 9.4.1 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 9.4.1 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, $E°_{\text{cell}}$ 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 9.4.1 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 9.4.2: 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 9.4.1.

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.

Exercise

Use the data in Table 9.4.1 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

$$\begin{aligned} \mathrm{I_2(s) + 2\,Br^-(aq)} &\longrightarrow \mathrm{2\,I^-(aq) + Br_2(l)} \qquad E_{\text{cell}} = -0.5518\ \mathrm{V\ (nonspontaneous)} \\ \mathrm{Br_2(s) + 2\,I^-(aq)} &\longrightarrow \mathrm{2\,Br^-(aq) + I_2(l)} \qquad E^\circ_{\text{cell}} = +0.5518\ \mathrm{V\ (spontaneous)} \end{aligned}$$

This page titled 9.4: Electrode and Cell Potentials is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **17.3: Electrode and Cell Potentials** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.5: 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, ΔG°, 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}:

$$\Delta G^\circ = w_{\text{max}} = w_{\text{elec}}$$

The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\Delta G^\circ = w_{\text{elec}} = -nFE^\circ_{\text{cell}}$$

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:

$$\Delta G^\circ = -RT\ln K = -nFE^\circ_{\text{cell}} \tag{9.5.1}$$

with

$$E^\circ_{\text{coll}} = \left(\frac{RT}{nF}\right)\ln K$$

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 9.5.1, and a table correlating reaction spontaneity to values of these properties is provided in Table 9.5.1.

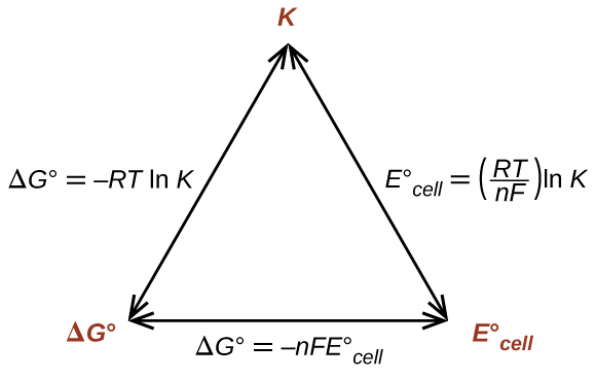


Figure 9.5.1: Graphic depicting the relation between three important thermodynamic properties.

Table 9.5.1

K	$\Delta G°$	$E°_{\text{cell}}$	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 9.5.1: 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.

$$2\,\text{Ag}^+(\text{aq}) + \text{Fe}(\text{s}) \rightleftharpoons 2\,\text{Ag}(\text{s}) + \text{Fe}^{2+}(\text{aq})$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Appendix L.

anode:	$\text{Fe}(\text{s}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + 2\,\text{e}^-$	$E^o_{\text{Fe}^{2+}/\text{Fe}} = -0.447\ \text{V}$
cathode:	$2 \times (\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s}))$	$E^o_{\text{Ag}^+/\text{Ag}} = +0.7996\ \text{V}$
cell:	$\text{Fe}(\text{s}) + 2\,\text{Ag}^+(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + 2\,\text{Ag}(\text{s})$	$E^o_{\text{cell}} = +1.2247\ \text{V}$

with

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^o_{\text{Fe}^{2+}/\text{Fe}} - E^o_{\text{Ag}^+/\text{Ag}} = +1.2247\ \text{V}$$

With $n = 2$, the equilibrium constant is then

$$E^\circ_{\text{cell}} = \frac{0.0592V}{n}\log K$$

$$K = 10^{n\times E^\circ_{\text{cal}}/0.0592V}$$

$$= 10^{2\times 1.247V/0.0592V}$$

$$= 10^{42.128}$$

$$= 1.3\times 10^{42}$$

The standard free energy is then Equation 9.5.1

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$= -2\times 96,485\frac{C}{mol}\times 1.247\frac{J}{C} = -240.6\frac{kJ}{mol}$$

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 9.5.1

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn(s)} + 2\,\text{Cu}^{2+}\text{(aq)} \rightleftharpoons \text{Sn}^{2+}\text{(aq)} + 2\,\text{Cu}^{+}\text{(aq)}$$

Answer

Spontaneous

$n = 2$

$E^\circ_{\text{cell}} = +0.291V$

$[\Delta G^\circ = -56.2\frac{kJ}{mol}$

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**:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT\ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

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:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592V}{n}\log Q \tag{9.5.2}$$

Example 9.5.2: 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:	$\mathrm{Co(s) \longrightarrow Co^{2+}(aq) + 2\,e^-}$	$E^o_{\mathrm{Co^{2+}/Co}} = -0.28\ \mathrm{V}$
cathode:	$\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)}$	$E^o_{\mathrm{Fe^{+}/Fe}} = -0.447\ \mathrm{V}$
cell:	$\mathrm{Co(s) + Fe^{2+}(Aq) \longrightarrow Fe(s) + Co^{2+}(aq)}$	$E^o_{\mathrm{cell}} = -0.17\ \mathrm{V}$

with

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.447V - (-0.28V) = -0.17V$$

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

$$Q = \frac{\left[\mathrm{Co^{2+}}\right]}{\left[\mathrm{Fe^{2+}}\right]} = \frac{0.15M}{1.94M} = 0.077$$

them Q and n are substituted into Equation \red{Nernst at room temperature}

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592\ \mathrm{V}}{n}\log Q \\ &= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log 0.077 \\ &= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} \\ &= -0.14\ \mathrm{V} \end{aligned}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Exercise 9.5.2

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 9.5.3: 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:

anode:	$\mathrm{Zn(s) \longrightarrow Zn^{2+}(aq,\ 0.10\ M) + 2\,e^-}$	$E^o_{\mathrm{Co^{2+}/Co}} = -0.7618\ \mathrm{V}$
cathode:	$\mathrm{Zn^{2+}(aq,\ 0.50\ M) + 2\,e^- \longrightarrow Zn(s)}$	$E^o_{\mathrm{Fe^{+}/Fe}} = -0,7618\ \mathrm{V}$
cell:	$\mathrm{\cancel{Zn(s)} + Zn^{2+}(aq,\ 0.50\ M) \longrightarrow Zn^{2+}(aq,\ 0.10\ M) + \cancel{Zn(s)}}$	$E^o_{\mathrm{cell}} = 0\ \mathrm{V}$

Substituting into the Nernst equation (Equation 9.5.2),

$$E_{\mathrm{cell}} = 0.000\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log\frac{0.10}{0.50} = +0.021\ \mathrm{V}$$

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 ($E_{\mathrm{cathode}} > E_{\mathrm{anode}}$).

? Exercise 9.5.1

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; $[Zn^{2+}]_{\mathrm{cathode}} = [Zn^{2+}]_{\mathrm{anode}}$ = 0.30 *M*

This page titled 9.5: Potential, Free Energy, and Equilibrium is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **17.4: Potential, Free Energy, and Equilibrium** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.6: 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 9.6.1):

$$\mathrm{Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)}$$

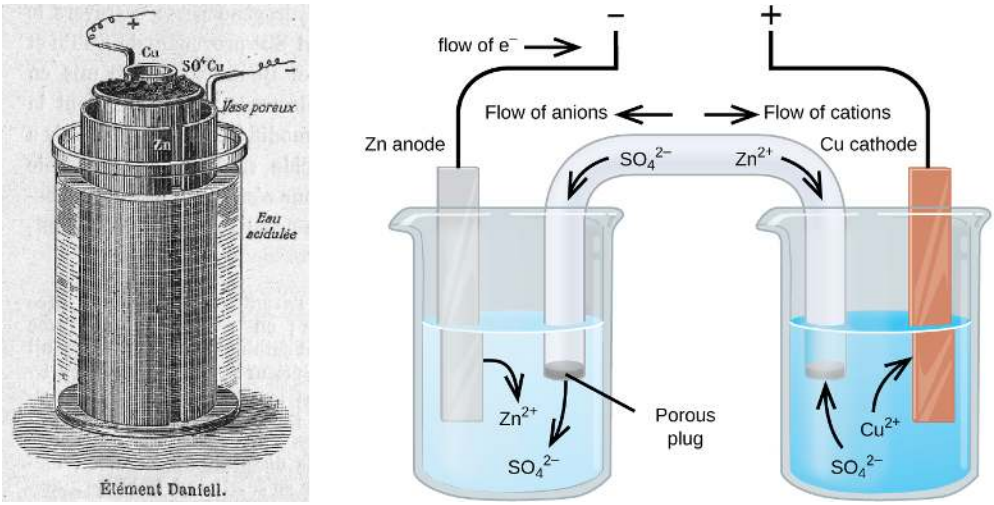


Figure 9.6.1: Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell's content and to serve as a salt bridge to the 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:

$$\mathrm{Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-} \qquad \text{(anode)}$$

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.

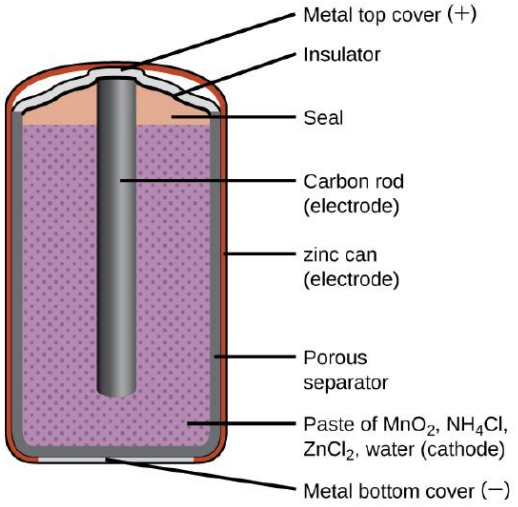


Figure 9.6.2: A schematic diagram shows a typical dry cell.

Link to Learning

Visit this site to learn more about zinc-carbon batteries.

Alkaline batteries (Figure 9.6.3) 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:	$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$	$E_{cell} = +1.43\ V$

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.

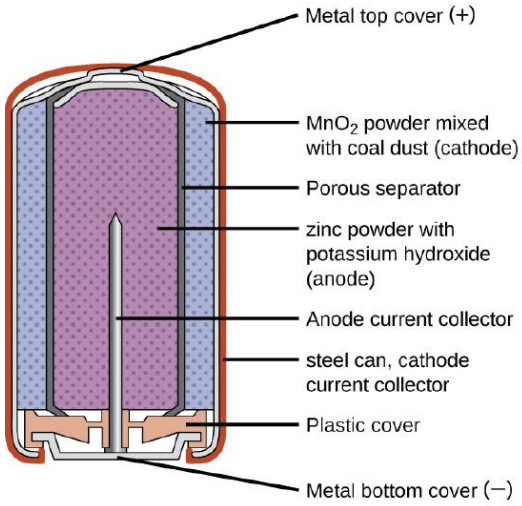


Figure 9.6.3: Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.

Link to Learning

Visit this site to learn more about alkaline batteries.

Rechargeable (Secondary) Batteries

Nickel-cadmium, or NiCd, batteries (Figure 9.6.4) 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.

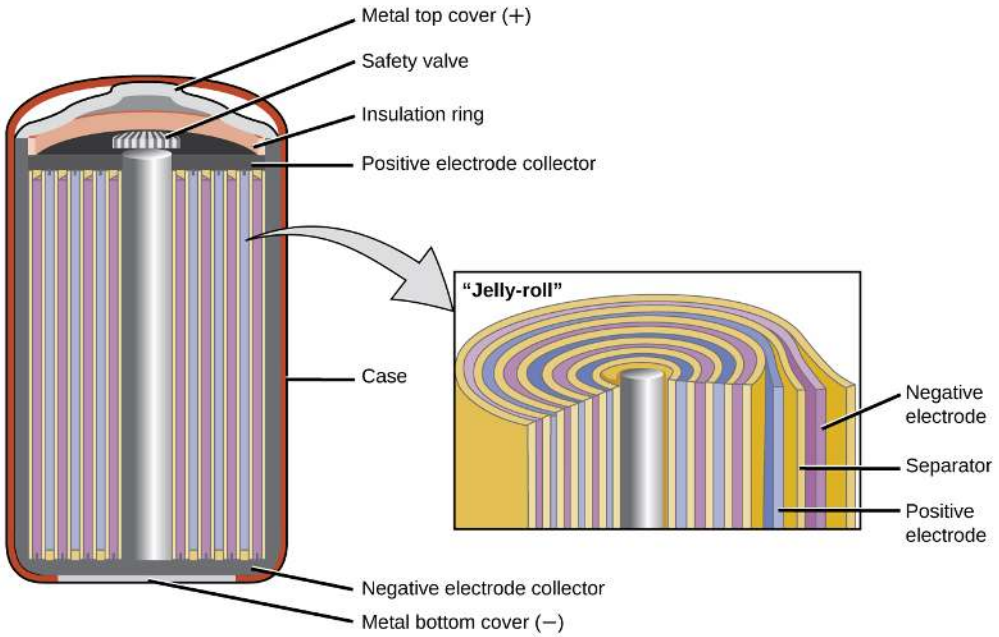


Figure 9.6.4: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Link to Learning

Visit this site for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries (Figure 9.6.5) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{lll} \text{anode:} & \mathrm{LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-} & \\ \text{cathode:} & \mathrm{x\,Li^+ + x\,e^- + x\,C_6 \longrightarrow x\,LiC_6} & \\ \hline \text{cell:} & \mathrm{LiCoO_2 + x\,C_6 \longrightarrow Li_{1-x}CoO_2 + x\,LiC_6} & E_{\text{cell}} \approx +3.7\,\text{V} \end{array}$$

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.

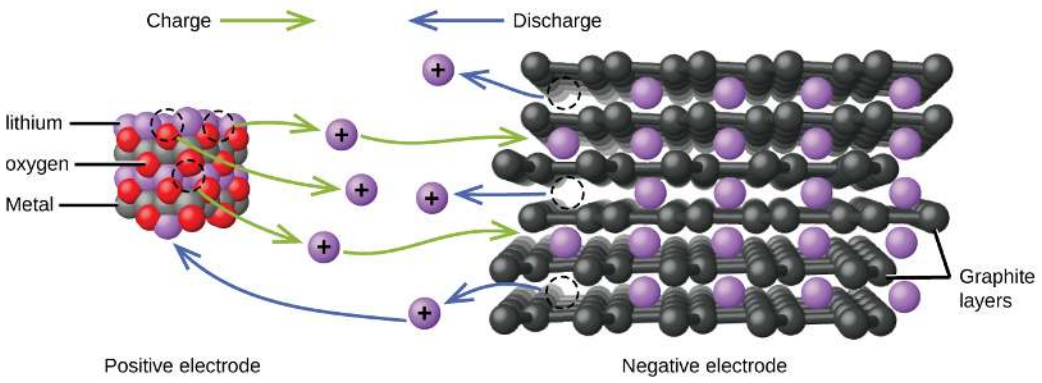


Figure 9.6.5: In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.

Link to Learning

Visit this site for more information about lithium ion batteries.

The lead acid battery (Figure 9.6.6) 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

$$\begin{array}{ll} \text{anode:} & \mathrm{Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-} \\ \text{cathode:} & \mathrm{PbO_2(s) + HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)} \\ \hline \text{cell:} & \mathrm{Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l)} \qquad E_{\text{cell}} \approx +2\text{ V} \end{array}$$

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.

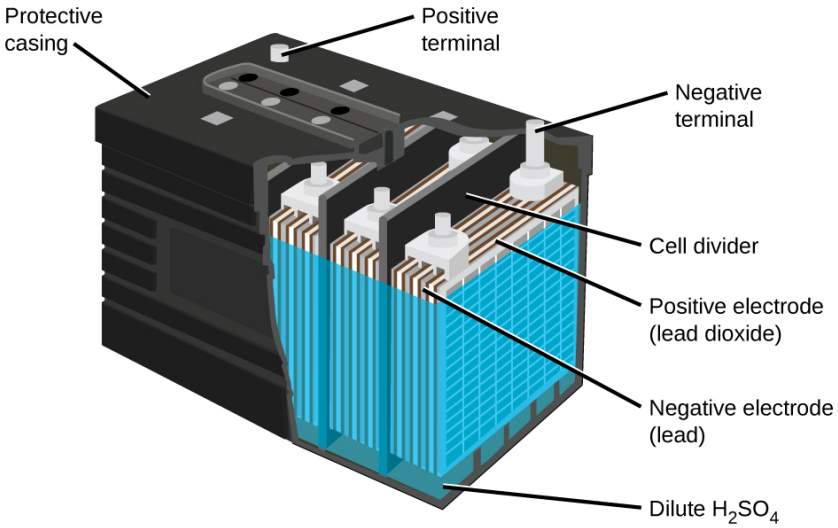


Figure 9.6.6: The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

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:

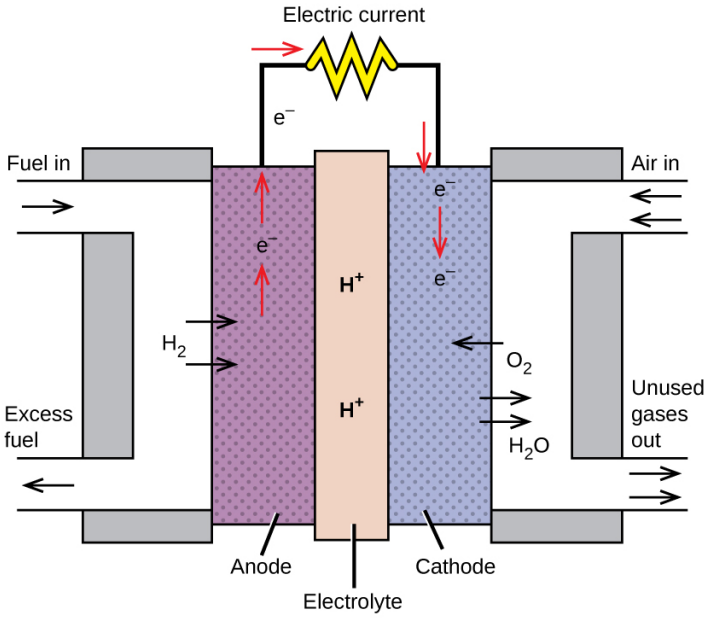


Figure 9.6.7: In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.

anode:	$2\,H_2(g) \longrightarrow 4\,H^+(aq) + 4\,e^-$
cathode:	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(g)$
cell:	$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad E_{cell} \approx +1.2\,V$

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 9.6: Batteries and Fuel Cells is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

- **17.5: Batteries and Fuel Cells** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.7: 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 9.7.1). 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

$$2\,Cu(s) + \tfrac{1}{2}O_2(g) \longrightarrow Cu_2O(s) \qquad \text{(red)}$$

$$2\,Cu_2O(s) + \tfrac{1}{2}O_2(g) \longrightarrow 2\,CuO(s) \qquad \text{(black)}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, atmospheric sulfur trioxide, carbon dioxide, and water all reacted with the CuO:

$$2\,CuO(s) + CO_2(g) + H_2O(l) \longrightarrow Cu_2CO_3(OH)_2(s) \qquad \text{(green)}$$

$$3\,CuO(s) + 2\,CO_2(g) + H_2O(l) \longrightarrow Cu_2(CO_3)_2(OH)_2(s) \qquad \text{(blue)}$$

$$4\,CuO(s) + SO_3(g) + 3\,H_2O(l) \longrightarrow Cu_4SO_4(OH)_6(s) \qquad \text{(green)}$$

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 9.7.1: (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 9.7.1. The relevant redox reactions are described by the following equations:

anode:	$\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-}$	$E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V}$
cathode:	$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)}$	$E^\circ_{\mathrm{O_2/O^{2-}}} = +1.23\ \mathrm{V}$
overall:	$\mathrm{2\,Fe(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l)}$	$E^\circ_{\mathrm{cell}} = +1.67\ \mathrm{V}$

Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:

$$\mathrm{4\,Fe^{2+}(aq) + O_2(g) + (4 + 2\,x)\,H_2O(l) \longrightarrow 2\,Fe_2O_3 \cdot x\,H_2O(s) + 8\,H^+(aq)}$$

The 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.

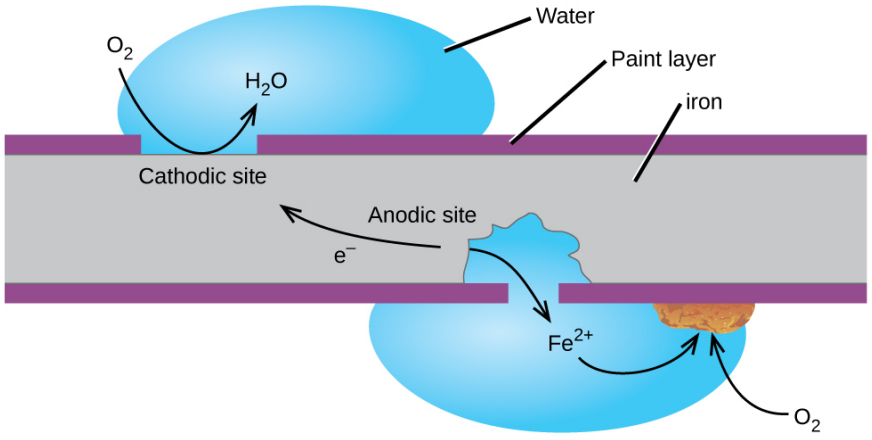


Figure 9.7.2: Corrosion can occur when a painted iron or steel surface is exposed to the environment by a scratch through the paint. A galvanic cell results that may be approximated by the simplified cell schematic Fe(*s*) | $Fe^{2+}(aq)$ ||$O_2(aq)$, $H_2O(l)$ | Fe(*s*).

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 9.7.3). 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.

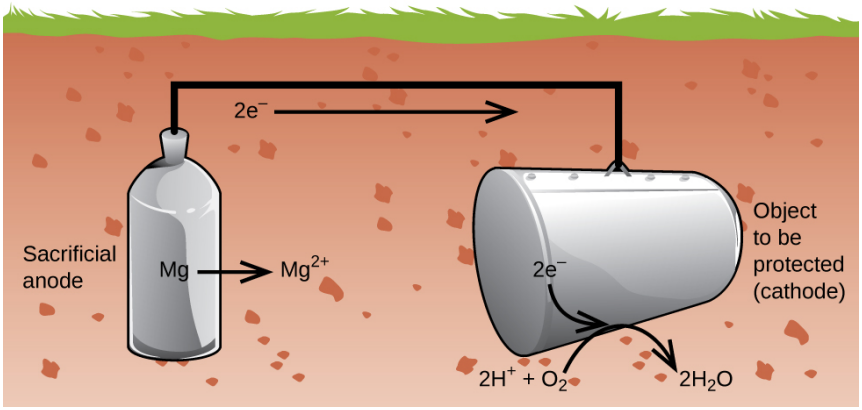


Figure 9.7.3: Cathodic protection is a useful approach to electrochemically preventing corrosion of underground storage tanks.

This page titled 9.7: Corrosion is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

9.8: 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 9.8.1. The reactions associated with this process are:

$$\begin{array}{lll} \text{oxidation:} & 2\,Cl^-(l) & \longrightarrow Cl_2(g) + 2e^- \\ + \quad \text{reduction:} & Na^+(l) + e^- & \longrightarrow Na(l) \\ \hline \text{cell:} & 2\,Cl^-(l) + 2\,Na^+(l) & \longrightarrow 2\,Na(l) + Cl_2(g) + 2e^- \end{array}$$

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.

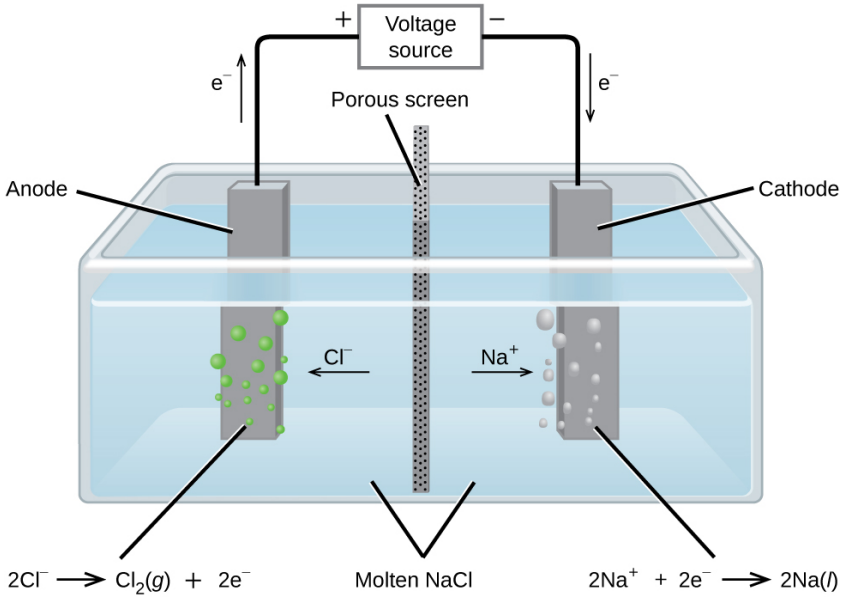


Figure 9.8.1: Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the *Downs process* for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.

The Electrolysis of Water

Water may be electrolytically decomposed in a cell similar to the one illustrated in Figure 9.8.2. 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

	oxidation:	$2\,H_2(l)$	$\longrightarrow O_2(g) + 4\,H^+ + 4\,e^-$	$E^o_{anode} = +1.299\ V$
+	reduction:	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	$E^o_{anode} = 0\ V$
	cell:	$2\,H_2O(l)$	$\longrightarrow 2\,H_2(g) + O_2(g$	$E^o_{cell} = -1.299\ V$

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.

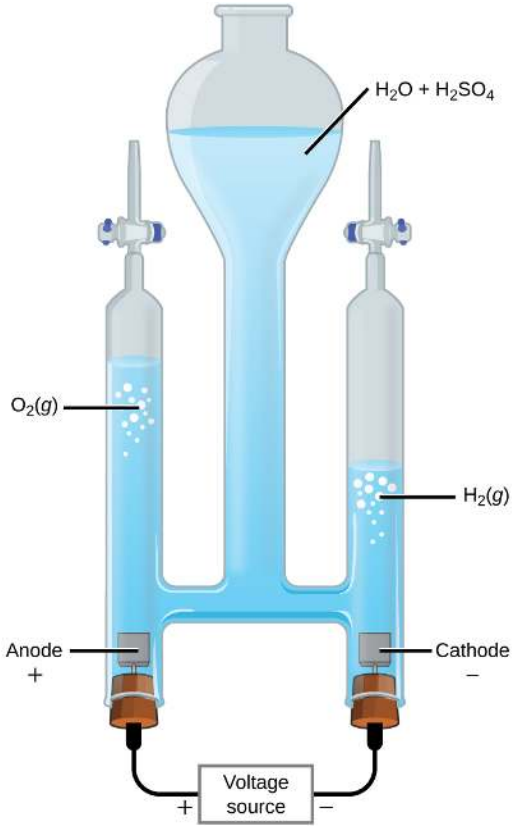


Figure 9.8.2: The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.

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 9.8.3).

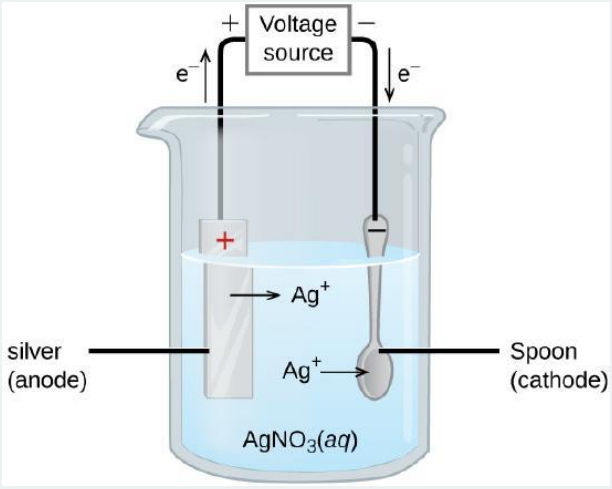


Figure 9.8.3: This schematic shows an electrolytic cell for silver plating eating utensils.

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

$$Ag(s) \longrightarrow Ag^+(aq) + e^- \qquad (anode)$$

and reduction of silver ion at the (spoon) cathode:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad (cathode)$$

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

$$\mathrm{M^{n^+}(aq) + n\,e^- \longrightarrow M(s)}$$

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 9.8.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for 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

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad \text{(cathode)}$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass } Ag = 0.3817 \text{ mol } \mathrm{e^-} \times \frac{1 \text{ mol Ag}}{1 \text{ mol } \mathrm{e^-}} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 41.19 \text{ g Ag}$$

Exercise 9.8.1

Aluminum metal can be made from aluminum(III) ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 25.0 A passed through the solution for 15.0 minutes?

Answer

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$$

0.0777 mol Al = 2.10 g Al.

Example 9.8.2: 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:

$$Q = 4.56molCr \times \frac{3mole^-}{1molCr} \times \frac{96485C}{mole^-} = 1.32 \times 10^6 C$$

Finally, if this charge is passed at a rate of 33.46 C/s, the required time is:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6 C}{33.46 C/s} = 3.95 \times 10^4 s = 11.0hr$$

Exercise 9.8.2

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 9.8: Electrolysis is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

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

9.9: 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

---

This page titled 9.9: Key Terms is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

9.10: Key Equations

$$\Delta G = -nFE_{\text{cell}}$$

$$Q = I\,t = n\,F$$

This page titled 9.10: Key Equations is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

9.11: 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.

This page titled 9.11: Summary is shared under a not declared license and was authored, remixed, and/or curated by OpenStax.

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

9.12: Exercises

1.

Identify each half-reaction below as either oxidation or reduction.

(a) $\mathrm{Fe}^{3}_{+} + 3\mathrm{e}^{-}$

(b) $\mathrm{Cr} \longrightarrow \mathrm{Cr}^{3}{+}{+} + 3\mathrm{e}^{-}$

(c) $\mathrm{MnO_4}^{2}{-} \longrightarrow \mathrm{MnO_4}^{-} + \mathrm{e}^{-}$

(d) $\mathrm{Li}^{+} + \mathrm{e}^{-} \longrightarrow \mathrm{Li}$

2.

Identify each half-reaction below as either oxidation or reduction.

(a) $\mathrm{Cl}^{-} \longrightarrow \mathrm{Cl_2}$

(b) $\mathrm{Mn}^{2+} \longrightarrow \mathrm{MnO_2}$

(c) $\mathrm{H_2} \longrightarrow \mathrm{H}^{+}$

(d) $\mathrm{NO_3}^{-}$

3.

Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

(a) $\mathrm{Ca} \longrightarrow \mathrm{Ca}^{2}{+}{+} + 2\mathrm{e}^{-},\ \mathrm{F_2} + 2\mathrm{e}^{-} \longrightarrow 2\mathrm{F}{-}$

(b) $\mathrm{Li} \longrightarrow \mathrm{Li}{+}{+}\mathrm{e}^{-},\ \mathrm{Cl_2} + 2\mathrm{e}^{-} \longrightarrow 2\mathrm{Cl}{-}$

(c) $\mathrm{Fe} \longrightarrow \mathrm{Fe}^{3}{+}{+} + 3\mathrm{e}^{-},\ \mathrm{Br_2} + 2\mathrm{e}^{-} \longrightarrow 2\mathrm{Br}{-}$

(d) $\mathrm{Ag} \longrightarrow \mathrm{Ag}^{+} + \mathrm{e}^{-},\ \mathrm{MnO_4}^{-} + 4\mathrm{H}^{+} + 3\mathrm{e}^{-} \longrightarrow \mathrm{MnO_2} + 2\mathrm{H_2O}$

4.

Balance the equations below assuming they occur in an acidic solution.

(a) $\mathrm{H_2O_2} + \mathrm{Sn}^{2+} \longrightarrow \mathrm{H_2O} + \mathrm{Sn}^{4+}$

(b) $\mathrm{PbO_2} + \mathrm{Hg} \longrightarrow \mathrm{Hg_2}^{2+} + \mathrm{Pb}^{2+}$

(c) $\mathrm{Al} + \mathrm{Cr_2O_7}^{2-} \longrightarrow \mathrm{Al}^{3+} + \mathrm{Cr}^{3+}$

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) $\mathrm{SO_3}^{2}{-}(aq) + \mathrm{Cu(OH)_2}(s) \longrightarrow \mathrm{SO_4}^{2}{-}(aq) + \mathrm{Cu(OH)}(s)$

(b) $\mathrm{O_2}(g) + \mathrm{Mn(OH)_2}(s) \longrightarrow \mathrm{MnO_2}(s)$

(c) $\mathrm{NO_3}^{-}(aq) + \mathrm{H_2}(g) \longrightarrow \mathrm{NO}(g)$

(d) $\mathrm{Al}(s) + \mathrm{CrO_4}^{2-}(aq) \longrightarrow \mathrm{Al(OH)_3}(s) + \mathrm{Cr(OH)_4}^{-}(aq)$

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) $\mathrm{Mg}(s) + \mathrm{Ni}^{2}_{+}(aq) \longrightarrow \mathrm{Mg}^{2}+(aq) + \mathrm{Ni}(s)$

(b) $2\mathrm{Ag}+(aq) + \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2}+(aq) + 2\mathrm{Ag}(s)$

(c) $\mathrm{Mn}(s) + \mathrm{Sn}(^{3}_{\mathrm{NO}})_{2}(aq) \longrightarrow \mathrm{Mn}(^{3}_{\mathrm{NO}})_{2}(aq) + \mathrm{Sn}(s)$

(d) $3\mathrm{CuNO}_{3}(aq) + \mathrm{Au}(\mathrm{NO}_{3})_{3}(aq) \longrightarrow 3\mathrm{Cu}(\mathrm{NO}_{3})_{2}(aq) + \mathrm{Au}(s)$

12.

Assuming the schematics below represent galvanic cells as written, identify the half-cell reactions occurring in each.

(a) $\mathrm{Mg}(s)\,|\,\mathrm{Mg}^{2+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s)$

(b) $\mathrm{Ni}(s)\,|\,\mathrm{Ni}^{2+}(aq)\,\|\,\mathrm{Ag}^{+}(aq)\,|\,\mathrm{Ag}(s)$

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) $\mathrm{Al}(s) + \mathrm{Zr}^{4}_{+}(aq) \longrightarrow \mathrm{Al}^{3}+(aq) + \mathrm{Zr}(s)$

(b) $\mathrm{Ag}^{+}(aq) + \mathrm{NO}(g) \longrightarrow \mathrm{Ag}(s) + {\mathrm{NO}_{3}}^{-}(aq)$ (acidic solution)

(c) ${\mathrm{SiO}_{3}}^{2-}(aq) + \mathrm{Mg}(s) \longrightarrow \mathrm{Si}(s) + \mathrm{Mg(OH)}_{2}(s)$ (basic solution)

(d) ${\mathrm{ClO}_{3}}^{-}(aq) + \mathrm{MnO}_{2}(s) \longrightarrow \mathrm{Cl}^{-}(aq) + {\mathrm{MnO}_{4}}^{-}(aq)$ (basic solution)

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 $\mathrm{Pt(NO_3)_2}$ forms Pt metal, while in the other half-cell, Cu metal goes into a $\mathrm{Cu(NO_3)_2}$ solution with all solute concentrations 1 *M*.

(b) The cathode consists of a gold electrode in a 0.55 *M* $\mathrm{Au(NO_3)_3}$ solution and the anode is a magnesium electrode in 0.75 *M* $\mathrm{Mg(NO_3)_2}$ solution.

(c) One half-cell consists of a silver electrode in a 1 *M* $\mathrm{AgNO_3}$ solution, and in the other half-cell, a copper electrode in 1 *M* $\mathrm{Cu(NO_3)_2}$ is oxidized.

17.

Why is a salt bridge necessary in galvanic cells like the one in Figure 16.3?

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) $\mathrm{Mg}(s) + \mathrm{Ni}^{2}_{+}(aq) \longrightarrow \mathrm{Mg}^{2}{+}(aq) + \mathrm{Ni}(s)$

(b) $2\mathrm{Ag}{+}(aq) + \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2}{+}(aq) + 2\mathrm{Ag}(s)$

(c) $\mathrm{Mn}(s) + \mathrm{Sn}(^{3}_{\mathrm{NO}})_2(aq) \longrightarrow \mathrm{Mn}(^{3}_{\mathrm{NO}})_2(aq) + \mathrm{Sn}(s)$

(d) $3\mathrm{Fe}(\mathrm{NO}_3)_2(aq) + \mathrm{Au}(\mathrm{NO}_3)_3(aq) \longrightarrow 3\mathrm{Fe}(\mathrm{NO}_3)_3(aq) + \mathrm{Au}(s)$

22.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

(a) $\mathrm{Mn}(s) + \mathrm{Ni}^{2+}(aq) \longrightarrow \mathrm{Mn}^{2+}(aq) + \mathrm{Ni}(s)$

(b) $3\mathrm{Cu}^{2+}(aq) + 2\mathrm{Al}(s) \longrightarrow 2\mathrm{Al}^{3+}(aq) + 3\mathrm{Cu}(s)$

(c) $\mathrm{Na}(s) + \mathrm{LiNO}_3(aq) \longrightarrow \mathrm{NaNO}_3(aq) + \mathrm{Li}(s)$

(d) $\mathrm{Ca}(\mathrm{NO}_3)_2(aq) + \mathrm{Ba}(s) \longrightarrow \mathrm{Ba}(\mathrm{NO}_3)_2(aq) + \mathrm{Ca}(s)$

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.

$\mathrm{Cu}(s) \,|\, \mathrm{Cu}^{2+}(aq) \,\|\, \mathrm{Au}^{3+}(aq) \,|\, \mathrm{Au}(s)$

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.
$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g)\,|\,\mathrm{H^+}(aq)\|\mathrm{Br_2}(aq),\ \mathrm{Br^-}(aq)\,|\,\mathrm{Pt}(s)$

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) $\mathrm{Hg}(l) + \mathrm{S^{2-}}(aq,\ 0.10\ M) + 2\mathrm{Ag^+}(aq,\ 0.25\ M) \longrightarrow 2\mathrm{Ag}(s) + \mathrm{HgS}(s)$

(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 bromide ion (1.0 *M*) is being oxidized to aqueous bromine (0.11 *M*) and a half-cell in which $\mathrm{Al^{3+}}$ (0.023 *M*) is being reduced to aluminum metal.

30.

Determine Δ*G* and Δ*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) $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$

(b) $\mathrm{CdS}(s) \rightleftharpoons \mathrm{Cd^{2+}}(aq) + \mathrm{S^{2-}}(aq)$ at 377 K

(c) $\mathrm{Hg^{2+}}(aq) + 4\mathrm{Br^-}(aq) \rightleftharpoons [\mathrm{HgBr_4}]^{2-}(aq)$

(d) $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{OH^-}(aq)$ at 25 °C

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: $\mathrm{Cu}(s) + 2\mathrm{Ag}^{+}(aq) \longrightarrow 2\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq)$.

(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 $(E^{\circ}_{Al^{3+}/Al} = -2.07\ \mathrm{V})$ is more easily oxidized than iron $(E^{\circ}_{Fe^{3+}/Fe} = -0.477\ \mathrm{V})$, 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 16.19 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 9.12: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax.

CHAPTER OVERVIEW

10: Appendices

10.1: Appendix A- The Periodic Table
10.2: Appendix B- Essential Mathematics
10.3: Appendix C- Units and Conversion Factors
10.4: Appendix D- Fundamental Physical Constants
10.5: Appendix E- Water Properties
10.6: Appendix F- Composition of Commercial Acids and Bases
10.7: Appendix G- Standard Thermodynamic Properties for Selected Substances
10.8: Appendix H- Ionization Constants of Weak Acids
10.9: Appendix I- Ionization Constants of Weak Bases
10.10: Appendix J- Solubility Products
10.11: Appendix K- Formation Constants for Complex Ions
10.12: Appendix L- Standard Electrode (Half-Cell) Potentials
10.13: Appendix M- Half-Lives for Several Radioactive Isotopes
10.14: Answer Keys
10.14.1: Chapter 1 - Radioactivity and Nuclear Chemistry
10.14.2: Chapter 2 - Chemical Bonding and Molecular Geometry
10.14.3: Chapter 3 - Advanced Theories of Covalent Bonding
10.14.4: Chapter 4 - Thermochemistry
10.14.5: Chapter 5 - Thermodynamics
10.14.6: Chapter 6 - Fundamental Equilibrium Concepts
10.14.7: Chapter 7 - Acid-Base Equilibria
10.14.8: Chapter 8 - Kinetics
10.14.9: Chapter 9 - Electrochemistry

This page titled 10: Appendices 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.

10.1: Appendix A- The Periodic Table

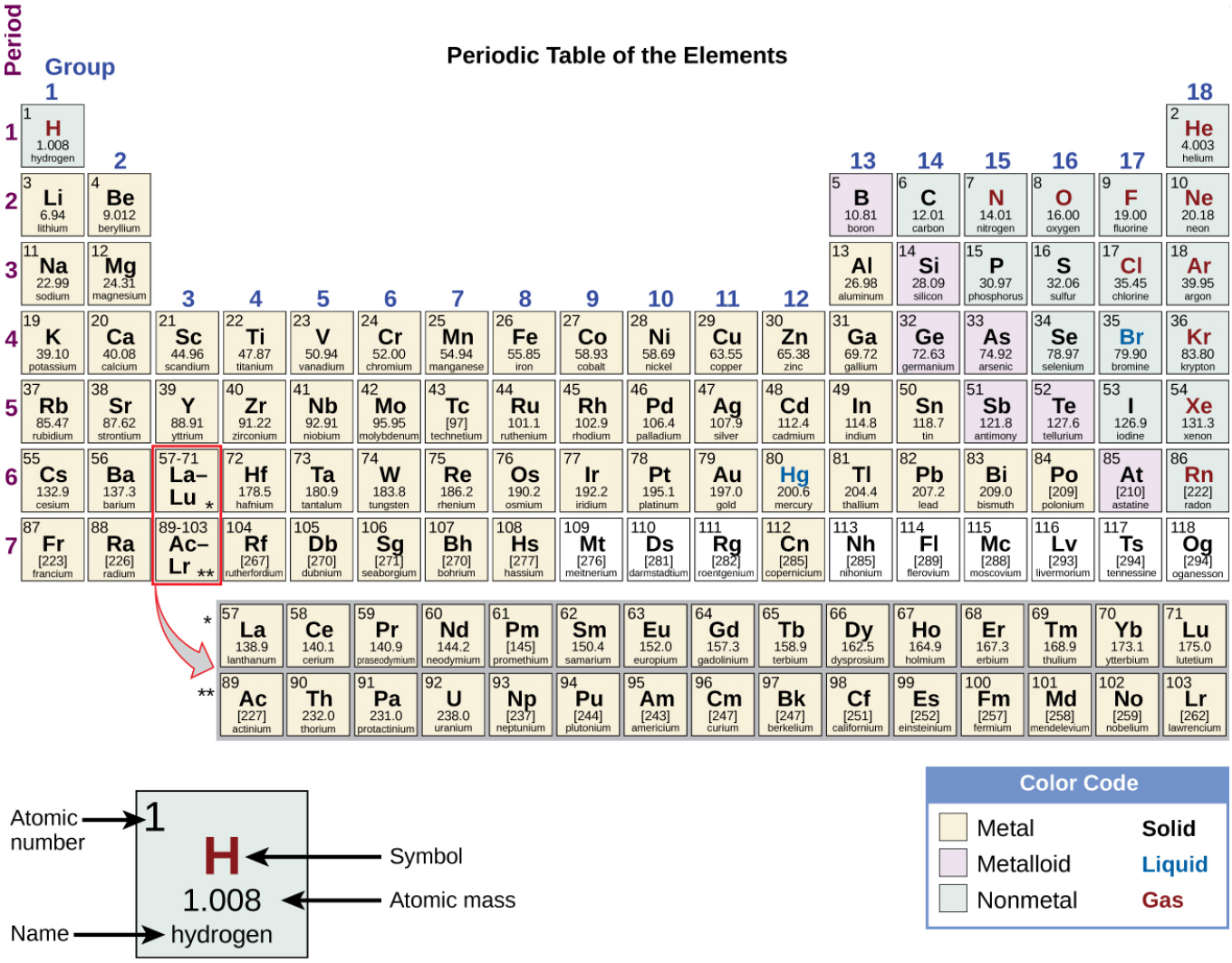


Figure A1

This page titled 10.1: Appendix A- The Periodic Table 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.

10.2: Appendix B- Essential Mathematics

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$$\begin{aligned} 1000 &= 1 \times 10^{3} \\ 100 &= 1 \times 10^{2} \\ 10 &= 1 \times 10^{1} \\ 1 &= 1 \times 10^{0} \\ 0.1 &= 1 \times 10^{-1} \\ 0.001 &= 1 \times 10^{-3} \\ 2386 &= 2.386 \times 1000 = 2.386 \times 10^{3} \\ 0.123 &= 1.23 \times 0.1 = 1.23 \times 10^{-1} \end{aligned}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, 1,230,000,000 = 1.23 × 10^{9}, and 0.00000000036 = 3.6 × 10^{-10}.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 10.2.1: Adding Exponentials

Add 5.00 × 10^{-5} and 3.00 × 10^{-3}.

Solution

$$\begin{aligned} 3.00 \times 10^{-3} &= 300 \times 10^{-5} \\ (5.00 \times 10^{-5}) + (300 \times 10^{-5}) &= 305 \times 10^{-5} = 3.05 \times 10^{-3} \end{aligned}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 10.2.2: Subtracting Exponentials

Subtract 4.0 × 10^{-7} from 5.0 × 10^{-6}.

Solution

$$\begin{aligned} 4.0 \times 10^{-7} &= 0.40 \times 10^{-6} \\ (5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) &= 4.6 \times 10^{-6} \end{aligned}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Exercise 10.2.3: Multiplying Exponentials

Multiply 4.2 × 10^{-8} by 2.0 × 10^{3}.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^{3}) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Exercise 10.2.4: Dividing Exponentials

Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Exercise 10.2.5: Squaring Exponentials

Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2\times(-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Exercise 10.2.6: Cubing Exponentials

Cube the number 2×10^{4}.

Solution

$$(2 \times 10^{4})^3 = 2 \times 2 \times 2 \times 10^{3\times4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Exercise 10.2.7: Finding the Square Root of Exponentials

Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the

computation (indicated by underscoring in the following example).

Exercise 10.2.8: Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

$$\begin{array}{r} 4.38\underline{3}\ \text{g} \\ +\ 0.00\underline{2}\underline{3}\ \text{g} \\ \hline 4.38\underline{5}\ \text{g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Exercise 10.2.9: Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

$$0.623\underline{8} \times 6.\underline{6} = 4.\underline{1}$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.001	10^{-3}	−3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers. \[\log xy= \log x + \log y, \textrm{ and }\ln xy=\ln x + \ln y \nonumber \]
2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers. \[\log\dfrac{x}{y}=\log x-\log y,\textrm{ and } \ln\dfrac{x}{y}=\ln x-\ln y \nonumber \]
3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

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

Solving Quadratic Equations Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (*x*-*y*) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

Exercise 10.2.10

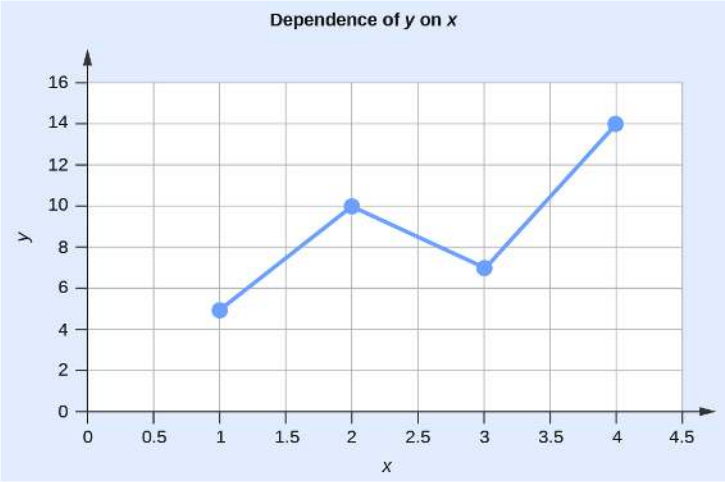
Graphing the Dependence of y on x

Table for Exercise 10

x	y
1	5
2	10
3	7

x	y
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x.



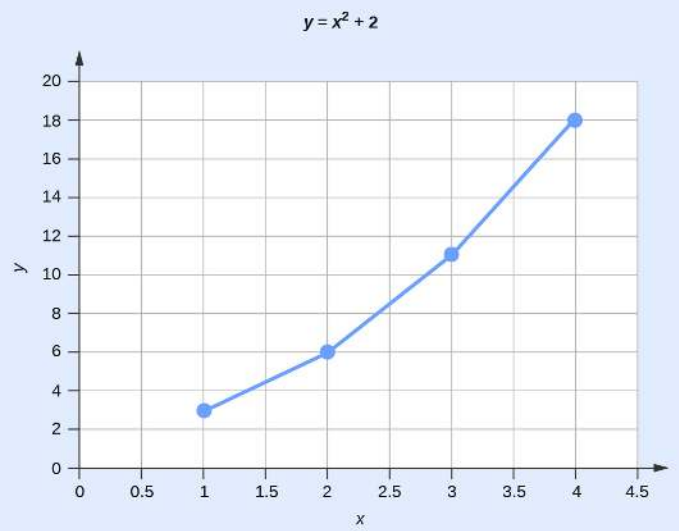
If the function that describes the dependence of y on x is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Exercise 10.2.11

Plotting Data Pairs If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

Table for Exercise 11

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



This page titled 10.2: Appendix B- Essential Mathematics 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.

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

10.3: Appendix C- Units and Conversion Factors

Units of Length

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume

Units of Volume			
liter (L)	= 0.001 m^3 (exact, definition) = 1000 cm^3 (exact, definition) = 1.057 (US) quarts	liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm^3 (exact, definition)	dry quart	= 1.1012 L
microliter (µL)	= 10^{-6} L (exact, definition) = 10^{-3} cm^3 (exact, definition)	cubic foot (US)	= 28.316 L

Units of Mass

Units of Mass			
gram (g)	= 0.001 kg (exact, definition)	ounce (oz) (avoirdupois)	= 28.35 g
milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy

Units of Energy	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[1]

Units of Pressure

Units of Pressure

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10^5 Pa (exact, definition) = 10^5 kg m^{-1} s^{-2} (exact, definition)

Footnotes

1. 1 BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

This page titled 10.3: Appendix C- Units and Conversion Factors 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.

- **22.11: Units and Conversion Factors** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.4: Appendix D- Fundamental Physical Constants

Table: Fundamental Physical Constants

Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
	1 u = $1.66053906660 \times 10^{-24}$ g
	1 g = $6.0221407621 \times 10^{23}$ u
Avogadro's number	$6.02214076 \times 10^{23}$ mol^{-1}
Boltzmann's constant (k)	1.380649×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
fundamental unit of charge (e) (charge on electron)	$1.602176634 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093897 \times 10^{-31}$ kg
	5.485799×10^{-4} u
Faraday's constant (F)	9.6485309×10^{4} C mol^{-1}
gas constant (R)	8.205784×10^{-2} L atm mol^{-1} K^{-1} = 8.314510 J mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 0 °C	22.41409 L mol^{-1}
molar volume of an ideal gas, 1 bar, 0 °C	22.71108 L mol^{-1}
neutron rest mass (m_n)	$1.6749274 \times 10^{-27}$ kg
	1.0086649 u
Planck's constant (h)	$6.62607015 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726231 \times 10^{-27}$ kg
	1.0072765 u
Rydberg constant (R)	$1.0973731534 \times 10^{7}$ m^{-1} = $2.1798736 \times 10^{-18}$ J
speed of light (in vacuum) (c)	2.99792458×10^{8} m s^{-1}

This page titled 10.4: Appendix D- Fundamental Physical 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.

- **Appendix D: Fundamental Physical Constants** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.5: Appendix E- Water Properties

Table E1: Water Density (g/mL) at Different Temperatures (°C)

Temperature	Density (g/mL)
0	0.9998395
4	0.9999720 (density maximum)
10	0.9997026
15	0.9991026
20	0.9982071
22	0.9977735
25	0.9970479
30	0.9956502
40	0.9922
60	0.9832
80	0.9718
100	0.9584

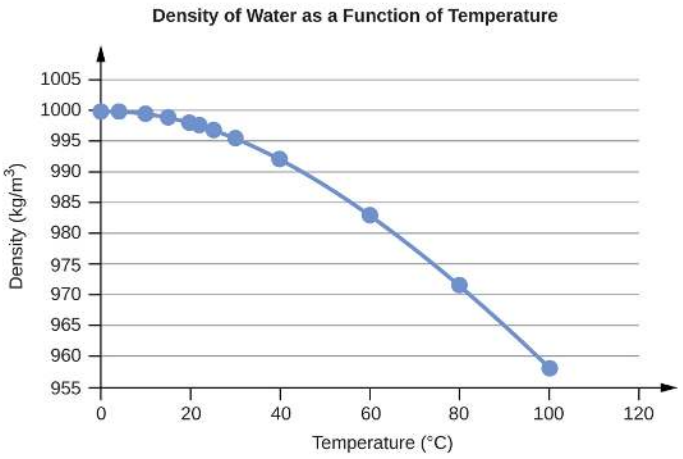


Table E2: Water Vapor Pressure at Different Temperatures (°C)

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71
95	633.9	84512.82
100	760.0	101324.7

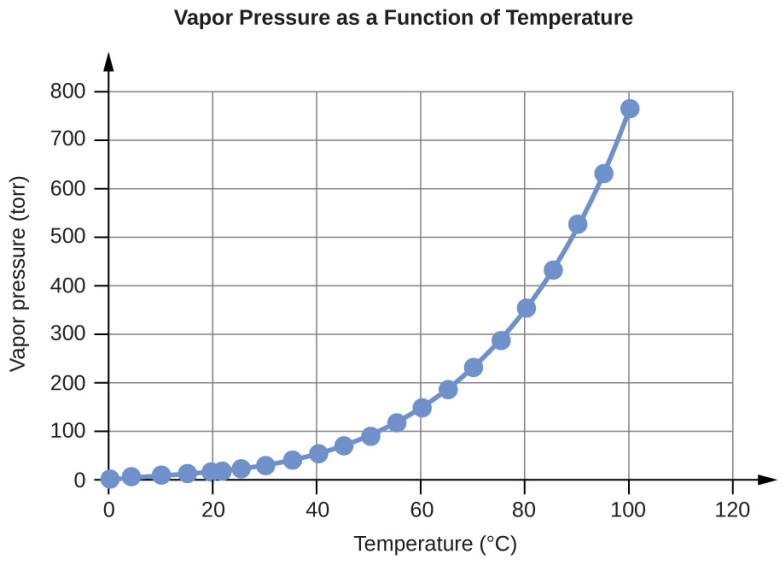


Table E3: Water K_w and pK_w at Different Temperatures (°C)

Temperature	K_w 10^{-14}	pK_w[1]
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33

Temperature	K_w 10^{-14}	pK_w [1]
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25

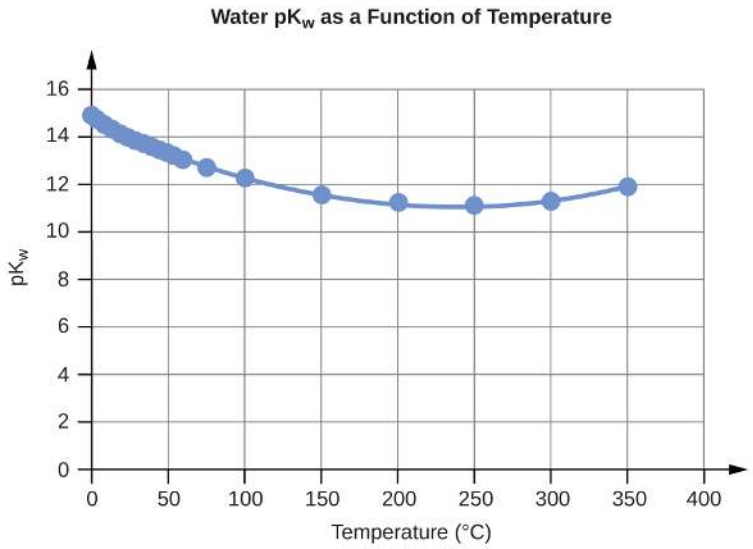


Table E4: Specific Heat Capacity for Water

$C°(H_2O(l)) = 4.184\ J{\cdot}g^{-1}{\cdot}°C^{-1}$
$C°(H_2O(s)) = 1.864\ J{\cdot}K^{-1}{\cdot}g^{-1}$
$C°(H_2O(g)) = 2.093\ J{\cdot}K^{-1}{\cdot}g^{-1}$

Table E5: Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Table E6: Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

$K_f = 1.86°C·kg·mol^{-1}$ (cryoscopic constant)
$K_b = 0.51°C·kg·mol^{-1}$ (ebullioscopic constant)

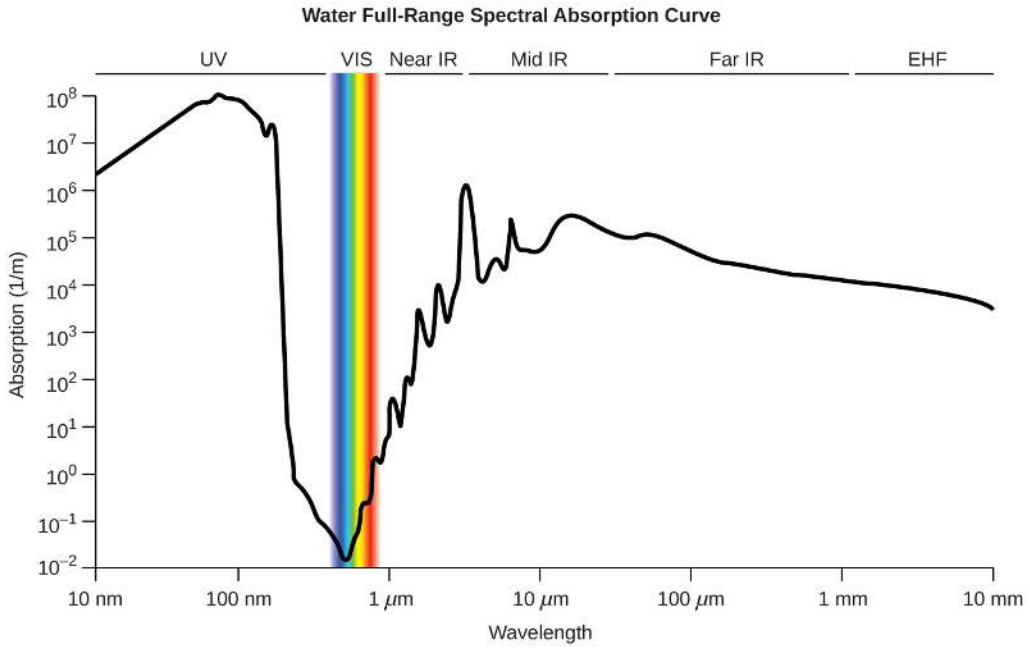


Figure E1: The plot shows the extent of light absorption versus wavelength for water. Absorption is reported in reciprocal meters and corresponds to the inverse of the distance light may travel through water before its intensity is diminished by 1/*e* (~37%).

Footnotes

- 1 $pK_w = -\log_{10}(K_w)$

This page titled 10.5: Appendix E- Water Properties 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.

- **Appendix E: Water Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.6: Appendix F- Composition of Commercial Acids and Bases

Table F1: Composition of Commercial Acids and Bases

Acid or Base[1]	Density (g/mL)[2]	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4
aqueous ammonia[3]	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

Footnotes

- 1Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.
- 2This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.
- 3This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.

This page titled 10.6: Appendix F- Composition of Commercial 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.

- **Appendix F: Composition of Commercial Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.7: Appendix G- Standard Thermodynamic Properties for Selected Substances

Table G1: Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f°(kJ mol^{-1})	S°(J K^{-1} mol^{-1})
aluminum			
Al(*s*)	0	0	28.3
Al(*g*)	324.4	285.7	164.54
$Al^{3+}(aq)$	–531	–485	–321.7
$Al_2O_3(s)$	–1676	–1582	50.92
$AlF_3(s)$	–1510.4	–1425	66.5
$AlCl_3(s)$	–704.2	–628.8	110.67
$AlCl_3 \cdot 6H_2O(s)$	–2691.57	–2269.40	376.56
$Al_2S_3(s)$	–724.0	–492.4	116.9
$Al_2(SO_4)_3(s)$	–3445.06	–3506.61	239.32
antimony			
Sb(*s*)	0	0	45.69
Sb(*g*)	262.34	222.17	180.16
$Sb_4O_6(s)$	–1440.55	–1268.17	220.92
$SbCl_3(g)$	–313.8	–301.2	337.80
$SbCl_5(g)$	–394.34	–334.29	401.94
Sb_2S_3(s)	–174.89	–173.64	182.00
$SbCl_3$(s)	–382.17	–323.72	184.10
SbOCl(s)	–374.0	—	—
arsenic			
As(*s*)	0	0	35.1
As(*g*)	302.5	261.0	174.21
$As_4(g)$	143.9	92.4	314
$As_4O_6(s)$	–1313.94	–1152.52	214.22
$As_2O_5(s)$	–924.87	–782.41	105.44
$AsCl_3(g)$	–261.50	–248.95	327.06
$As_2S_3(s)$	–169.03	–168.62	163.59
$AsH_3(g)$	66.44	68.93	222.78
$H_3AsO_4(s)$	–906.3	—	—
barium			
Ba(*s*)	0	0	62.5
Ba(*g*)	180	146	170.24
$Ba^{2+}(aq)$	–537.6	–560.8	9.6

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
BaO(*s*)	–548.0	–520.3	72.1
$BaCl_2$(*s*)	–855.0	–806.7	123.7
$BaSO_4$(*s*)	–1473.2	–1362.3	132.2
beryllium			
Be(*s*)	0	0	9.50
Be(*g*)	324.3	286.6	136.27
BeO(*s*)	–609.4	–580.1	13.8
bismuth			
Bi(*s*)	0	0	56.74
Bi(*g*)	207.1	168.2	187.00
Bi_2O_3(*s*)	–573.88	–493.7	151.5
$BiCl_3$(*s*)	–379.07	–315.06	176.98
Bi_2S_3(*s*)	–143.1	–140.6	200.4
boron			
B(*s*)	0	0	5.86
B(*g*)	565.0	521.0	153.4
B_2O_3(*s*)	–1273.5	–1194.3	53.97
B_2H_6(*g*)	36.4	87.6	232.1
H_3BO_3(*s*)	–1094.33	–968.92	88.83
BF_3(*g*)	–1136.0	–1119.4	254.4
BCl_3(*g*)	–403.8	–388.7	290.1
$B_3N_3H_6$(*l*)	–540.99	–392.79	199.58
HBO_2(*s*)	–794.25	–723.41	37.66
bromine			
Br_2(*l*)	0	0	152.23
Br_2(*g*)	30.91	3.142	245.5
Br(*g*)	111.88	82.429	175.0
Br^-(*aq*)	–120.9	–102.82	80.71
BrF_3(*g*)	–255.60	–229.45	292.42
HBr(*g*)	–36.3	–53.43	198.7
cadmium			
Cd(*s*)	0	0	51.76
Cd(*g*)	112.01	77.41	167.75
Cd^{2+}(*aq*)	–75.90	–77.61	–73.2
CdO(*s*)	–258.2	–228.4	54.8

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$CdCl_2(s)$	–391.5	–343.9	115.3
$CdSO_4(s)$	–933.3	–822.7	123.0
$CdS(s)$	–161.9	–156.5	64.9
calcium			
$Ca(s)$	0	0	41.6
$Ca(g)$	178.2	144.3	154.88
$Ca^{2+}(aq)$	–542.96	–553.04	–55.2
$CaO(s)$	–634.9	–603.3	38.1
$Ca(OH)_2(s)$	–985.2	–897.5	83.4
$CaSO_4(s)$	–1434.5	–1322.0	106.5
$CaSO_4 \cdot 2H_2O(s)$	–2022.63	–1797.45	194.14
$CaCO_3(s)$ (calcite)	–1220.0	–1081.4	110.0
$CaSO_3 \cdot H_2O(s)$	–1752.68	–1555.19	184.10
carbon			
$C(s)$ (graphite)	0	0	5.740
$C(s)$ (diamond)	1.89	2.90	2.38
$C(g)$	716.681	671.2	158.1
$CO(g)$	–110.52	–137.15	197.7
$CO_2(g)$	–393.51	–394.36	213.8
$CO_3^{2-}(aq)$	–677.1	–527.8	–56.9
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3^-(aq)$	–691.11	–587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
cesium			
$Cs^+(aq)$	–248	–282.0	133
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$Cl^-(aq)$	–167.2	–131.2	56.5
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$CrO_4^{2-}(aq)$	–881.2	–727.8	50.21
$Cr_2O_7^{2-}(aq)$	–1490.3	–1301.1	261.9
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrO_3(s)$	–589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	–1806.7	—	—
cobalt			

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Co(s)	0	0	30.0
$Co^{2+}(aq)$	–67.4	–51.5	–155
$Co^{3+}(aq)$	92	134	–305.0
CoO(s)	–237.9	–214.2	52.97
$Co_3O_4(s)$	–910.02	–794.98	114.22
$Co(NO_3)_2(s)$	–420.5	—	—
copper			
Cu(s)	0	0	33.15
Cu(g)	338.32	298.58	166.38
$Cu^+(aq)$	51.9	50.2	–26
$Cu^{2+}(aq)$	64.77	65.49	–99.6
CuO(s)	–157.3	–129.7	42.63
$Cu_2O(s)$	–168.6	–146.0	93.14
CuS(s)	–53.1	–53.6	66.5
$Cu_2S(s)$	–79.5	–86.2	120.9
$CuSO_4(s)$	–771.36	–662.2	109.2
$Cu(NO_3)_2(s)$	–302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
F(g)	79.4	62.3	158.8
$F^-(aq)$	–332.6	–278.8	–13.8
$F_2O(g)$	24.7	41.9	247.43
HF(g)	–273.3	–275.4	173.8
hydrogen			
$H_2(g)$	0	0	130.7
H(g)	217.97	203.26	114.7
$H^+(aq)$	0	0	0
$OH^-(aq)$	–230.0	–157.2	–10.75
$H_3O^+(aq)$	–285.8		69.91
$H_2O(l)$	–285.83	–237.1	70.0
$H_2O(g)$	–241.82	–228.59	188.8
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(g)$	–136.3	–105.6	232.7
HF(g)	–273.3	–275.4	173.8
HCl(g)	–92.307	–95.299	186.9

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
HBr(*g*)	–36.3	–53.43	198.7
HI(*g*)	26.48	1.70	206.59
H_2S(*g*)	–20.6	–33.4	205.8
H_2Se(*g*)	29.7	15.9	219.0
HNO_3	–206.64	—	—
iodine			
I_2(*s*)	0	0	116.14
I_2(*g*)	62.438	19.3	260.7
I(*g*)	106.84	70.2	180.8
I^-(*aq*)	–55.19	–51.57	11.13
IF(*g*)	95.65	–118.49	236.06
ICl(*g*)	17.78	–5.44	247.44
IBr(*g*)	40.84	3.72	258.66
IF_7(*g*)	–943.91	–818.39	346.44
HI(*g*)	26.48	1.70	206.59
iron			
Fe(*s*)	0	0	27.3
Fe(*g*)	416.3	370.7	180.5
Fe^{2+}(*aq*)	–89.1	–78.90	–137.7
Fe^{3+}(*aq*)	–48.5	–4.7	–315.9
Fe_2O_3(*s*)	–824.2	–742.2	87.40
Fe_3O_4(*s*)	–1118.4	–1015.4	146.4
$Fe(CO)_5$(*l*)	–774.04	–705.42	338.07
$Fe(CO)_5$(*g*)	–733.87	–697.26	445.18
$FeCl_2$(*s*)	–341.79	–302.30	117.95
$FeCl_3$(*s*)	–399.49	–334.00	142.3
FeO(*s*)	–272.0	–255.2	60.75
$Fe(OH)_2$(*s*)	–569.0	–486.5	88.
$Fe(OH)_3$(*s*)	–823.0	–696.5	106.7
FeS(*s*)	–100.0	–100.4	60.29
Fe_3C(*s*)	25.10	20.08	104.60
lead			
Pb(*s*)	0	0	64.81
Pb(*g*)	195.2	162.	175.4
Pb^{2+}(*aq*)	–1.7	–24.43	10.5

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
PbO(*s*) (yellow)	–217.32	–187.89	68.70
PbO(*s*) (red)	–218.99	–188.93	66.5
$Pb(OH)_2(s)$	–515.9	—	—
PbS(*s*)	–100.4	–98.7	91.2
$Pb(NO_3)_2(s)$	–451.9	—	—
$PbO_2(s)$	–277.4	–217.3	68.6
$PbCl_2(s)$	–359.4	–314.1	136.0
lithium			
Li(*s*)	0	0	29.1
Li(*g*)	159.3	126.6	138.8
$Li^+(aq)$	–278.5	–293.3	13.4
LiH(*s*)	–90.5	–68.3	20.0
Li(OH)(*s*)	–487.5	–441.5	42.8
LiF(*s*)	–616.0	–587.5	35.7
$Li_2CO_3(s)$	–1216.04	–1132.19	90.17
magnesium			
$Mg^{2+}(aq)$	–466.9	–454.8	–138.1
manganese			
Mn(*s*)	0	0	32.0
Mn(*g*)	280.7	238.5	173.7
$Mn^{2+}(aq)$	–220.8	–228.1	–73.6
MnO(*s*)	–385.2	–362.9	59.71
$MnO_2(s)$	–520.03	–465.1	53.05
$Mn_2O_3(s)$	–958.97	–881.15	110.46
$Mn_3O_4(s)$	–1378.83	–1283.23	155.64
$MnO_4^-(aq)$	–541.4	–447.2	191.2
$MnO_4^{2-}(aq)$	–653.0	–500.7	59
mercury			
Hg(*l*)	0	0	75.9
Hg(*g*)	61.4	31.8	175.0
$Hg^{2+}(aq)$		164.8	
$Hg^{2+}(aq)$	172.4	153.9	84.5
HgO(*s*) (red)	–90.83	–58.5	70.29
HgO(*s*) (yellow)	–90.46	–58.43	71.13
$HgCl_2(s)$	–224.3	–178.6	146.0

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$Hg_2Cl_2(s)$	–265.4	–210.7	191.6
HgS(*s*) (red)	–58.16	–50.6	82.4
HgS(*s*) (black)	–53.56	–47.70	88.28
$HgSO_4(s)$	–707.51	–594.13	0.00
nickel			
$Ni^{2+}(aq)$	–64.0	–46.4	–159
nitrogen			
$N_2(g)$	0	0	191.6
$N(g)$	472.704	455.5	153.3
$NO(g)$	90.25	87.6	210.8
$NO_2(g)$	33.2	51.30	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_3(g)$	83.72	139.41	312.17
$NO_3^-(aq)$	–205.0	–108.7	146.4
$N_2O_4(g)$	11.1	99.8	304.4
$N_2O_5(g)$	11.3	115.1	355.7
$NH_3(g)$	–45.9	–16.5	192.8
$NH_4^+(aq)$	–132.5	–79.31	113.4
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
$HNO_3(aq)$	–207.4	–110.5	146
oxygen			
$O_2(g)$	0	0	205.2
$O(g)$	249.17	231.7	161.1
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
P(g)	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$PO_4^{3-}(aq)$	–1277	–1019	–222
$HPO_3(s)$	–948.5	—	—
$HPO_4^{2-}(aq)$	–1292.1	–1089.3	–33
$H_2PO_4^{2-}(aq)$	–1296.3	–1130.4	90.4
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			
K(s)	0	0	64.7
K(g)	89.0	60.5	160.3
$K^+(aq)$	–252.4	–283.3	102.5
KF(s)	–576.27	–537.75	66.57
KCl(s)	–436.5	–408.5	82.6
rubidium			
$Rb^+(aq)$	–246	–282.2	124
silicon			
Si(s)	0	0	18.8
Si(g)	450.0	405.5	168.0
$SiO_2(s)$	–910.7	–856.3	41.5
$SiH_4(g)$	34.3	56.9	204.6
$H_2SiO_3(s)$	–1188.67	–1092.44	133.89
$H_4SiO_4(s)$	–1481.14	–1333.02	192.46
$SiF_4(g)$	–1615.0	–1572.8	282.8
$SiCl_4(l)$	–687.0	–619.8	239.7
$SiCl_4(g)$	–662.75	–622.58	330.62

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
SiC(*s*, *beta cubic*)	–73.22	–70.71	16.61
SiC(*s*, *alpha hexagonal*)	–71.55	–69.04	16.48
silver			
Ag(*s*)	0	0	42.55
Ag(*g*)	284.9	246.0	172.89
$Ag^+(aq)$	105.6	77.11	72.68
$Ag_2O(s)$	–31.05	–11.20	121.3
AgCl(*s*)	–127.0	–109.8	96.3
$Ag_2S(s)$	–32.6	–40.7	144.0
sodium			
Na(*s*)	0	0	51.3
Na(*g*)	107.5	77.0	153.7
$Na^+(aq)$	–240.1	–261.9	59
$Na_2O(s)$	–414.2	–375.5	75.1
NaCl(*s*)	–411.2	–384.1	72.1
strontium			
$Sr^{2+}(aq)$	–545.8	–557.3	–32.6
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
S(*g*)	278.81	238.25	167.82
$S^{2-}(aq)$	41.8	83.7	22
$SO_2(g)$	–296.83	–300.1	248.2
$SO_3(g)$	–395.72	–371.06	256.76
$SO_4^{2-}(aq)$	–909.3	–744.5	20.1
$S_2O_3^{2-}(aq)$	–648.5	–522.5	67
$H_2S(g)$	–20.6	–33.4	205.8
$HS^-(aq)$	–17.7	12.6	61.1
$H_2SO_4(l)$	–813.989	–690.00	156.90
$HSO_4^{2-}(aq)$	–885.75	–752.87	126.9
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
SO_2Cl_2(g)	–354.80	–310.45	311.83
tin			
Sn(s)	0	0	51.2
Sn(g)	301.2	266.2	168.5
SnO(s)	–285.8	–256.9	56.5
$SnO_2(s)$	–577.6	–515.8	49.0
$SnCl_4(l)$	–511.3	–440.1	258.6
$SnCl_4(g)$	–471.5	–432.2	365.8
titanium			
Ti(s)	0	0	30.7
Ti(g)	473.0	428.4	180.3
$TiO_2(s)$	–944.0	–888.8	50.6
$TiCl_4(l)$	–804.2	–737.2	252.4
$TiCl_4(g)$	–763.2	–726.3	353.2
tungsten			
W(s)	0	0	32.6
W(g)	849.4	807.1	174.0
$WO_3(s)$	–842.9	–764.0	75.9
zinc			
Zn(s)	0	0	41.6
Zn(g)	130.73	95.14	160.98
$Zn^{2+}(aq)$	–153.9	–147.1	–112.1
ZnO(s)	–350.5	–320.5	43.7
$ZnCl_2(s)$	–415.1	–369.43	111.5
ZnS(s)	–206.0	–201.3	57.7
$ZnSO_4(s)$	–982.8	–871.5	110.5
$ZnCO_3(s)$	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—

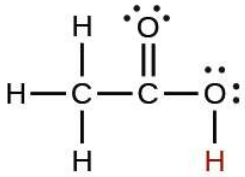
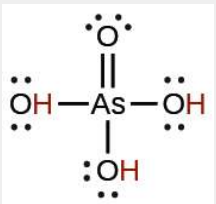
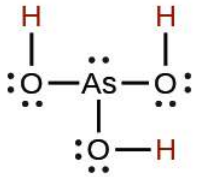
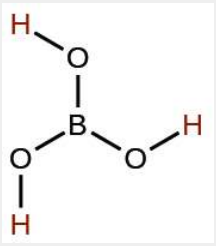
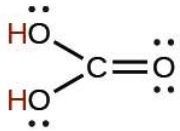
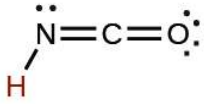
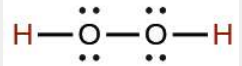
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
$[Co(NH_3)_5Cl]Cl_2$	–1017.1	–582.5	366.1
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

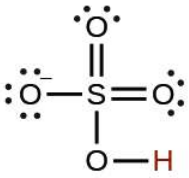
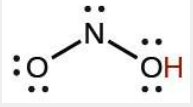
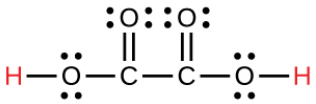
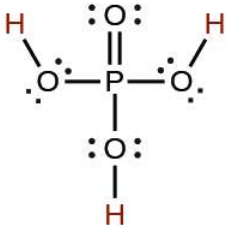
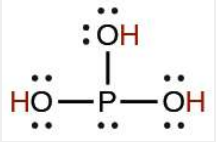
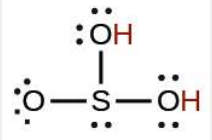
This page titled 10.7: Appendix G- Standard Thermodynamic Properties for Selected Substances is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by OpenStax via source content that was edited to the style and standards of the LibreTexts platform.

- **Appendix G: Standard Thermodynamic Properties for Selected Substances** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.8: Appendix H- Ionization Constants of Weak Acids

Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
acetic	$CH_3CO_2\mathbf{H}$	1.8×10^{-5}	
arsenic	$\mathbf{H_3}AsO_4$	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	
	$HAsO_4^{2-}$	5.1×10^{-12}	
arsenous	$\mathbf{H_3}AsO_3$	5.1×10^{-10}	
boric	$\mathbf{H_3}BO_3$	5.4×10^{-10}	
carbonic	$\mathbf{H_2}CO_3$	4.3×10^{-7}	
	HCO_3^-	4.7×10^{-11}	
cyanic	$\mathbf{H}CNO$	2×10^{-4}	
formic	$HCO_2\mathbf{H}$	1.8×10^{-4}	
hydrazoic	$\mathbf{H}N_3$	2.5×10^{-5}	
hydrocyanic	$\mathbf{H}CN$	4.9×10^{-10}	
hydrofluoric	$\mathbf{H}F$	3.5×10^{-4}	
hydrogen peroxide	$\mathbf{H_2}O_2$	2.4×10^{-12}	
hydrogen selenide	$\mathbf{H_2}Se$	1.29×10^{-4}	
	$\mathbf{H}Se^-$	1×10^{-12}	

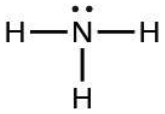
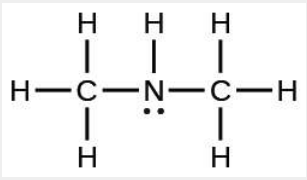
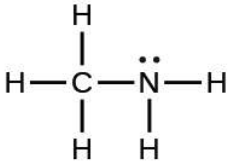
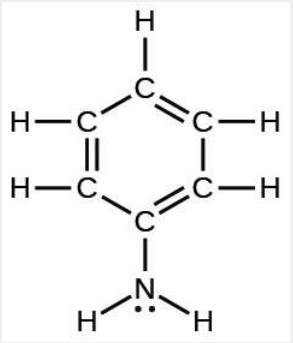
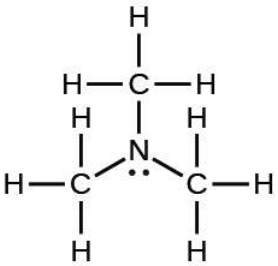
Acid	Formula	K_a at 25 °C	Lewis Structure
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	
	HTe^-	1.6×10^{-11}	
hypobromous	HBrO	2.8×10^{-9}	
hypochlorous	HClO	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	
oxalic	$H_2C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^-$	6.1×10^{-5}	
phosphoric	H_3PO_4	7.5×10^{-3}	
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

This page titled 10.8: Appendix H- Ionization Constants of Weak 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.

- **22.5: Ionization Constants of Weak Acids** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.9: Appendix I- Ionization Constants of Weak Bases

Ionization Constants of Weak Bases

Base	Lewis Structure	K_b at 25 °C
ammonia		1.8×10^{-5}
dimethylamine		5.9×10^{-4}
methylamine		4.4×10^{-4}
phenylamine (aniline)		4.3×10^{-10}
trimethylamine		6.3×10^{-5}

This page titled 10.9: Appendix I- Ionization Constants of Weak 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.

- **22.6: Ionization Constants of Weak Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.10: Appendix J- Solubility Products

Solubility Products

Substance	K_{sp} at 25 °C
aluminum	
$Al(OH)_3$	2×10^{-32}
barium	
$BaCO_3$	1.6×10^{-9}
$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}
$BaSO_4$	2.3×10^{-8}
$BaCrO_4$	8.5×10^{-11}
BaF_2	2.4×10^{-5}
$Ba(OH)_2 \cdot 8H_2O$	5.0×10^{-3}
$Ba_3(PO_4)_2$	6×10^{-39}
$Ba_3(AsO_4)_2$	1.1×10^{-13}
bismuth	
BiO(OH)	4×10^{-10}
BiOCl	1.8×10^{-31}
Bi_2S_3	1×10^{-97}
cadmium	
$Cd(OH)_2$	5.9×10^{-15}
CdS	1.0×10^{-28}
$CdCO_3$	5.2×10^{-12}
calcium	
$Ca(OH)_2$	1.3×10^{-6}
$CaCO_3$	8.7×10^{-9}
CaSO4·$2H_2O$	6.1×10^{-5}
$CaC_2O_4 \cdot H_2O$	1.96×10^{-8}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$CaHPO_4$	7×10^{-7}
CaF_2	4.0×10^{-11}
chromium	
$Cr(OH)_3$	6.7×10^{-31}
cobalt	
$Co(OH)_2$	2.5×10^{-16}
CoS(α)	5×10^{-22}
CoS(β)	3×10^{-26}

Substance	K_{sp} at 25 °C
$CoCO_3$	1.4×10^{-13}
$Co(OH)_3$	2.5×10^{-43}
copper	
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
CuI	1.27×10^{-12}
CuSCN	1.6×10^{-11}
Cu_2S	2.5×10^{-48}
$Cu(OH)_2$	2.2×10^{-20}
CuS	8.5×10^{-45}
$CuCO_3$	2.5×10^{-10}
iron	
$Fe(OH)_2$	1.8×10^{-15}
$FeCO_3$	2.1×10^{-11}
FeS	3.7×10^{-19}
$Fe(OH)_3$	4×10^{-38}
lead	
$Pb(OH)_2$	1.2×10^{-15}
PbF_2	4×10^{-8}
$PbCl_2$	1.6×10^{-5}
$PbBr_2$	4.6×10^{-6}
PbI_2	1.4×10^{-8}
$PbCO_3$	1.5×10^{-15}
PbS	7×10^{-29}
$PbCrO_4$	2×10^{-16}
$PbSO_4$	1.3×10^{-8}
$Pb_3(PO_4)_2$	1×10^{-54}
magnesium	
$Mg(OH)_2$	8.9×10^{-12}
$MgCO_3 \cdot 3H_2O$	*ca* 1×10^{-5}
$MgNH_4PO_4$	3×10^{-13}
MgF_2	6.4×10^{-9}
MgC_2O_4	7×10^{-7}
manganese	
$Mn(OH)_2$	2×10^{-13}

Substance	K_{sp} at 25 °C
$MnCO_3$	8.8×10^{-11}
MnS	2.3×10^{-13}
mercury	
$Hg_2O \cdot H_2O$	3.6×10^{-26}
Hg_2Cl_2	1.1×10^{-18}
Hg_2Br_2	1.3×10^{-22}
Hg_2I_2	4.5×10^{-29}
Hg_2CO_3	9×10^{-15}
Hg_2SO_4	7.4×10^{-7}
Hg_2S	1.0×10^{-47}
Hg_2CrO_4	2×10^{-9}
HgS	1.6×10^{-54}
nickel	
$Ni(OH)_2$	1.6×10^{-16}
$NiCO_3$	1.4×10^{-7}
NiS(α)	4×10^{-20}
NiS(β)	1.3×10^{-25}
potassium	
$KClO_4$	1.05×10^{-2}
K_2PtCl_6	7.48×10^{-6}
$KHC_4H_4O_6$	3×10^{-4}
silver	
$\frac{1}{2}Ag_2O(Ag^+ + OH^-)$	2×10^{-8}
AgCl	1.6×10^{-10}
AgBr	5.0×10^{-13}
AgI	1.5×10^{-16}
AgCN	1.2×10^{-16}
AgSCN	1.0×10^{-12}
Ag_2S	1.6×10^{-49}
Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	9.0×10^{-12}
$Ag_4Fe(CN)_6$	1.55×10^{-41}
Ag_2SO_4	1.2×10^{-5}
Ag_3PO_4	1.8×10^{-18}
strontium	

Substance	K_{sp} at 25 °C
$Sr(OH)_2 \cdot 8H_2O$	3.2×10^{-4}
$SrCO_3$	7×10^{-10}
$SrCrO_4$	3.6×10^{-5}
$SrSO_4$	3.2×10^{-7}
$SrC_2O_4 \cdot H_2O$	4×10^{-7}
thallium	
TlCl	1.7×10^{-4}
TlSCN	1.6×10^{-4}
Tl_2S	6×10^{-22}
$Tl(OH)_3$	6.3×10^{-46}
tin	
$Sn(OH)_2$	3×10^{-27}
SnS	1×10^{-26}
$Sn(OH)_4$	1.0×10^{-57}
zinc	
$ZnCO_3$	2×10^{-10}

This page titled 10.10: Appendix J- Solubility Products 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.

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

10.11: Appendix K- Formation Constants for Complex Ions

Formation Constants for Complex Ions

Equilibrium	K_f
$Al^{3+} + 6\,F^- \rightleftharpoons [AlF_6]^{3-}$	7×10^{19}
$Cd^{2+} + 4\,NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3×10^{7}
$Cd^{2+} + 4\,CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	3×10^{18}
$Co^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^{5}
$Co^{3+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	2.3×10^{33}
$Cu^{+} + 2\,CN \rightleftharpoons [Cu(CN)_2]^-$	1.0×10^{16}
$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.7×10^{13}
$Fe^{2+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.5×10^{35}
$Fe^{3+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	2×10^{43}
$Fe^{3+} + 6\,SCN^- \rightleftharpoons [Fe(SCN)_6]^{3-}$	3.2×10^{3}
$Hg^{2+} + 4\,Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.1×10^{16}
$Ni^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	2.0×10^{8}
$Ag^{+} + 2\,Cl^- \rightleftharpoons [AgCl_2]^-$	1.8×10^{5}
$Ag^{+} + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^-$	1×10^{21}
$Ag^{+} + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.7×10^{7}
$Zn^{2+} + 4\,CN^- \rightleftharpoons [Zn(CN)_4]^{2-}$	2.1×10^{19}
$Zn^{2+} + 4\,OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	2×10^{15}
$Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$	8.9×10^{2}
$Ag^{+} + 4\,SCN^- \rightleftharpoons [Ag(SCN)_4]^{3-}$	1.2×10^{10}
$Pb^{2+} + 4\,I^- \rightleftharpoons [PbI_4]^{2-}$	3.0×10^{4}
$Pt^{2+} + 4\,Cl^- \rightleftharpoons [PtCl_4]^{2-}$	1×10^{16}
$Cu^{2+} + 4\,CN \rightleftharpoons [Cu(CN)_4]^{2-}$	1.0×10^{25}
$Co^{2+} + 4\,SCN^- \rightleftharpoons [Co(SCN)_4]^{2-}$	1×10^{3}

This page titled 10.11: Appendix K- Formation Constants for Complex Ions 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.

- **22.3: Formation Constants for Complex Ions** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.12: Appendix L- Standard Electrode (Half-Cell) Potentials

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$\mathrm{Ag^+ + e^- \longrightarrow Ag}$	+0.7996
$\mathrm{AgCl + e^- \longrightarrow Ag + Cl^-}$	+0.22233
$\mathrm{[Ag(CN)_2]^- + e^- \longrightarrow Ag + 2\,CN^-}$	−0.31
$\mathrm{Ag_2CrO_4 + 2\,e^- \longrightarrow 2\,Ag + CrO_4^{2-}}$	+0.45
$\mathrm{[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2\,NH_3}$	+0.373
$\mathrm{[Ag(S_2O_3)_2]^{3+} + e^- \longrightarrow Ag + 2\,S_2O_3^{2-}}$	+0.017
$\mathrm{[AlF_6]^{3-} + 3\,e^- \longrightarrow Al + 6\,F^-}$	−2.07
$\mathrm{Al^{3+} + 3\,e^- \longrightarrow Al}$	−1.662
$\mathrm{Am^{3+} + 3\,e^- \longrightarrow Am}$	−2.048
$\mathrm{Au^{3+} + 3\,e^- \longrightarrow Au}$	+1.498
$\mathrm{Au^+ + e^- \longrightarrow Au}$	+1.692
$\mathrm{Ba^{2+} + 2\,e^- \longrightarrow Ba}$	−2.912
$\mathrm{Be^{2+} + 2\,e^- \longrightarrow Be}$	−1.847
$\mathrm{Br_2}(aq) + \mathrm{2\,e^- \longrightarrow 2\,Br^-}$	+1.0873
$\mathrm{Ca^{2+} + 2\,e^- \longrightarrow Ca}$	−2.868
$\mathrm{Ce^3 + 3\,e^- \longrightarrow Ce}$	−2.483
$\mathrm{Ce^{4+} + e^- \longrightarrow Ce^{3+}}$	+1.61
$\mathrm{Cd^{2+} + 2\,e^- \longrightarrow Cd}$	−0.4030
$\mathrm{[Cd(CN)_4]^{2-} + 2\,e^- \longrightarrow Cd + 4\,CN^-}$	−1.09
$\mathrm{[Cd(NH_3)_4]^{2+} + 2\,e^- \longrightarrow Cd + 4\,NH_3}$	−0.61
$\mathrm{CdS + 2\,e^- \longrightarrow Cd + S^{2-}}$	−1.17
$\mathrm{Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-}$	+1.35827
$\mathrm{ClO_4^- + H_2O + 2\,e^- \longrightarrow ClO_3^- + 2\,OH^-}$	+0.36
$\mathrm{ClO_3^- + H_2O + 2\,e^- \longrightarrow ClO_2^- + 2\,OH^-}$	+0.33
$\mathrm{ClO_2^- + H_2O + 2\,e^- \longrightarrow ClO^- + 2\,OH^-}$	+0.66
$\mathrm{ClO^- + H_2O + 2\,e^- \longrightarrow Cl^- + 2\,OH^-}$	+0.89
$\mathrm{ClO_4^- + 2\,H_3O^+ + 2\,e^- \longrightarrow ClO_3^- + 3\,H_2O}$	+1.189
$\mathrm{ClO_3^- + 3\,H_3O^+ + 2\,e^- \longrightarrow HClO_2 + 4\,H_2O}$	+1.21
$\mathrm{HClO + H_3O^+ + 2\,e^- \longrightarrow Cl^- + 2\,H_2O}$	+1.482
$\mathrm{HClO + H_3O^+ + e^- \longrightarrow \frac{1}{2}Cl_2 + 2\,H_2O}$	+1.611
$\mathrm{HClO_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow HClO + 3\,H_2O}$	+1.628
$\mathrm{Co^{3+} + e^- \longrightarrow Co^{2+}\ (2\ mol\ //\ H_2SO_4)}$	+1.83

Half-Reaction	$E°$ (V)
$\mathrm{Co^{2+} + 2\,e^- \longrightarrow Co}$	−0.28
$\mathrm{[Co(NH_3)_6]^{3+} + e^- \longrightarrow [Co(NH_3)_6]^{2+}}$	+0.1
$\mathrm{Co(OH)_3 + e^- \longrightarrow Co(OH)_2 + OH^-}$	+0.17
$\mathrm{Cr^3 + 3\,e^- \longrightarrow Cr}$	−0.744
$\mathrm{Cr^{3+} + e^- \longrightarrow Cr^{2+}}$	−0.407
$\mathrm{Cr^{2+} + 2\,e^- \longrightarrow Cr}$	−0.913
$\mathrm{[Cu(CN)_2]^- + e^- \longrightarrow Cu + 2\,CN^-}$	−0.43
$\mathrm{CrO_4^{2-} + 4\,H_2O + 3\,e^- \longrightarrow Cr(OH)_3 + 5\,OH^-}$	−0.13
$\mathrm{Cr_2O_7^{2-} + 14\,H_3O^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 21\,H_2O}$	+1.232
$\mathrm{[Cr(OH)_4]^- + 3\,e^- \longrightarrow Cr + 4\,OH^-}$	−1.2
$\mathrm{Cr(OH)_3 + 3\,e^- \longrightarrow Cr + 3\,OH^-}$	−1.48
$\mathrm{Cu^{2+} + e^- \longrightarrow Cu^+}$	+0.153
$\mathrm{Cu^{2+} + 2\,e^- \longrightarrow Cu}$	+0.34
$\mathrm{Cu^+ + e^- \longrightarrow Cu}$	+0.521
$\mathrm{F_2 + 2\,e^- \longrightarrow 2\,F^-}$	+2.866
$\mathrm{Fe^{2+} + 2\,e^- \longrightarrow Fe}$	−0.447
$\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}}$	+0.771
$\mathrm{[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}}$	+0.36
$\mathrm{Fe(OH)_2 + 2\,e^- \longrightarrow Fe + 2\,OH^-}$	−0.88
$\mathrm{FeS + 2\,e^- \longrightarrow Fe + S^{2-}}$	−1.01
$\mathrm{Ga^{3+} + 3\,e^- \longrightarrow Ga}$	−0.549
$\mathrm{Gd^{3+} + 3\,e^- \longrightarrow Gd}$	−2.279
$\mathrm{\frac{1}{2}H_2 + e^- \longrightarrow H^-}$	−2.23
$\mathrm{2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-}$	−0.8277
$\mathrm{H_2O_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow 4\,H_2O}$	+1.776
$\mathrm{2\,H_3O^+ + 2\,e^- \longrightarrow H_2 + 2\,H_2O}$	0.00
$\mathrm{HO_2^- + H_2O + 2\,e^- \longrightarrow 3\,OH^-}$	+0.878
$\mathrm{Hf^{4+} + 4\,e^- \longrightarrow Hf}$	−1.55
$\mathrm{Hg^{2+} + 2\,e^- \longrightarrow Hg}$	+0.851
$\mathrm{2\,Hg^{2+} + 2\,e^- \longrightarrow Hg_2^{2+}}$	+0.92
$\mathrm{Hg_2^{2+} + 2\,e^- \longrightarrow 2\,Hg}$	+0.7973
$\mathrm{[HgBr_4]^{2-} + 2\,e^- \longrightarrow Hg + 4\,Br^-}$	+0.21
$\mathrm{Hg_2Cl_2 + 2\,e^- \longrightarrow 2\,Hg + 2\,Cl^-}$	+0.26808
$\mathrm{[Hg(CN)_4]^{2-} + 2\,e^- \longrightarrow Hg + 4\,CN^-}$	−0.37

Half-Reaction	$E°$ (V)
$[HgI_4]^{2-} + 2e^- \longrightarrow Hg + 4I^-$	−0.04
$HgS + 2e^- \longrightarrow Hg + S^{2-}$	−0.70
$I_2 + 2e^- \longrightarrow 2I^-$	+0.5355
$In^{3+} + 3e^- \longrightarrow In$	−0.3382
$K^+ + e^- \longrightarrow K$	−2.931
$La^{3+} + 3e^- \longrightarrow La$	−2.52
$Li^+ + e^- \longrightarrow Li$	−3.04
$Lu^{3+} + 3e^- \longrightarrow Lu$	−2.28
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.185
$MnO_2 + 2H_2O + 2e^- \longrightarrow Mn(OH)_2 + 2OH^-$	−0.05
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.558
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.507
$Na^+ + e^- \longrightarrow Na$	−2.71
$Nd^{3+} + 3e^- \longrightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.257
$[Ni(NH_3)_6]^{2+} + 2e^- \longrightarrow Ni + 6NH_3$	−0.49
$NiO_2 + 4H^+ + 2e^- \longrightarrow Ni^{2+} + 2H_2O$	+1.593
$NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$	+0.49
$NiS + 2e^- \longrightarrow Ni + S^{2-}$	+0.76
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.957
$NO_3^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$	+0.92
$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^-$	+0.10
$Np^{3+} + 3e^- \longrightarrow Np$	−1.856
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.401
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	+0.695
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.1262
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.69
$PbS + 2e^- \longrightarrow Pb + S^{2-}$	−0.95
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e^- \longrightarrow Pd$	+0.987
$[PdCl_4]^{2-} + 2e^- \longrightarrow Pd + 4Cl^-$	+0.591

Half-Reaction	$E°$ (V)
$\mathrm{Pt^{2+} + 2\,e^- \longrightarrow Pt}$	+1.20
$\mathrm{[PtBr_4]^{2-} + 2\,e^- \longrightarrow Pt + 4\,Br^-}$	+0.58
$\mathrm{[PtCl_4]^{2-} + 2\,e^- \longrightarrow Pt + 4\,Cl^-}$	+0.755
$\mathrm{[PtCl_6]^{2-} + 2\,e^- \longrightarrow [PtCl_4]^{2-} + 2\,Cl^-}$	+0.68
$\mathrm{Pu^{3} + 3\,e^- \longrightarrow Pu}$	−2.03
$\mathrm{Ra^{2+} + 2\,e^- \longrightarrow Ra}$	−2.92
$\mathrm{Rb^{+} + e^- \longrightarrow Rb}$	−2.98
$\mathrm{[RhCl_6]^{3-} + 3\,e^- \longrightarrow Rh + 6\,Cl^-}$	+0.44
$\mathrm{S + 2\,e^- \longrightarrow S^{2-}}$	−0.47627
$\mathrm{S + 2\,H^+ + 2\,e^- \longrightarrow H_2S}$	+0.142
$\mathrm{Sc^{3+} + 3\,e^- \longrightarrow Sc}$	−2.09
$\mathrm{Se + 2\,H^+ + 2\,e^- \longrightarrow H_2Se}$	−0.399
$\mathrm{[SiF_6]^{2-} + 4\,e^- \longrightarrow Si + 6\,F^-}$	−1.2
$\mathrm{SiO_3^{2-} + 3\,H_2O + 4\,e^- \longrightarrow Si + 6\,OH^-}$	−1.697
$\mathrm{SiO_2 + 4\,H^+ + 4\,e^- \longrightarrow Si + 2\,H_2O}$	−0.86
$\mathrm{Sm^{3+} + 3\,e^- \longrightarrow Sm}$	−2.304
$\mathrm{Sn^{4+} + 2\,e^- \longrightarrow Sn^{2+}}$	+0.151
$\mathrm{Sn^{2+} + 2\,e^- \longrightarrow Sn}$	−0.1375
$\mathrm{[SnF_6]^{2-} + 4\,e^- \longrightarrow Sn + 6\,F^-}$	−0.25
$\mathrm{SnS + 2\,e^- \longrightarrow Sn + S^{2-}}$	−0.94
$\mathrm{Sr^{2+} + 2\,e^- \longrightarrow Sr}$	−2.89
$\mathrm{TeO_2 + 4\,H^+ + 4\,e^- \longrightarrow Te + 2\,H_2O}$	+0.593
$\mathrm{Th^{4+} + 4\,e^- \longrightarrow Th}$	−1.90
$\mathrm{Ti^{2+} + 2\,e^- \longrightarrow Ti}$	−1.630
$\mathrm{U^{3+} + 3\,e^- \longrightarrow U}$	−1.79
$\mathrm{V^{2+} + 2\,e^- \longrightarrow V}$	−1.19
$\mathrm{Y^{3+} + 3\,e^- \longrightarrow Y}$	−2.37
$\mathrm{Zn^{2+} + 2\,e^- \longrightarrow Zn}$	−0.7618
$\mathrm{[Zn(CN)_4]^{2-} + 2\,e^- \longrightarrow Zn + 4\,CN^-}$	−1.26
$\mathrm{[Zn(NH_3)_4]^{2+} + 2\,e^- \longrightarrow Zn + 4\,NH_3}$	−1.04
$\mathrm{Zn(OH)_2 + 2\,e^- \longrightarrow Zn + 2\,OH^-}$	−1.245
$\mathrm{[Zn(OH)_4]^{2} + 2\,e^- \longrightarrow Zn + 4\,OH^-}$	−1.199
$\mathrm{ZnS + 2\,e^- \longrightarrow Zn + S^{2-}}$	−1.40
$\mathrm{Zr^{4} + 4\,e^- \longrightarrow Zr}$	−1.539

This page titled 10.12: Appendix L- Standard Electrode (Half-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.

- **22.8: Standard Electrode (Half-Cell) Potentials** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.13: Appendix M- Half-Lives for Several Radioactive Isotopes

Half-Lives for Several Radioactive Isotopes

Isotope	Half-Life[1]	Type of Emission[2]	Isotope	Half-Life[3]	Type of Emission[4]
$^{14}_{6}\mathrm{C}$	5730 y	(β^-)	$^{210}_{83}\mathrm{Bi}$	5.01 d	(β^-)
$^{13}_{7}\mathrm{N}$	9.97 m	(β^+)	$^{212}_{83}\mathrm{Bi}$	60.55 m	$(\alpha \text{ or } \beta^-)$
$^{15}_{9}\mathrm{F}$	4.1×10^{-22} s	(p)	$^{210}_{84}\mathrm{Po}$	138.4 d	(α)
$^{24}_{11}\mathrm{Na}$	15.00 h	(β^-)	$^{212}_{84}\mathrm{Po}$	3×10^{-7} s	(α)
$^{32}_{15}\mathrm{P}$	14.29 d	(β^-)	$^{216}_{84}\mathrm{Po}$	0.15 s	(α)
$^{40}_{19}\mathrm{K}$	1.27×10^{9} y	$(\beta \text{ or } E.C.)$	$^{218}_{84}\mathrm{Po}$	3.05 m	(α)
$^{49}_{26}\mathrm{Fe}$	0.08 s	(β^+)	$^{215}_{85}\mathrm{At}$	1.0×10^{-4} s	(α)
$^{60}_{26}\mathrm{Fe}$	2.6×10^{6} y	(β^-)	$^{218}_{85}\mathrm{At}$	1.6 s	(α)
$^{60}_{27}\mathrm{Co}$	5.27 y	(β^-)	$^{220}_{86}\mathrm{Rn}$	55.6 s	(α)
$^{87}_{37}\mathrm{Rb}$	4.7×10^{10} y	(β^-)	$^{222}_{86}\mathrm{Rn}$	3.82 d	(α)
$^{90}_{38}\mathrm{Sr}$	29 y	(β^-)	$^{224}_{88}\mathrm{Ra}$	3.66 d	(α)
$^{115}_{49}\mathrm{In}$	5.1×10^{15} y	(β^-)	$^{226}_{88}\mathrm{Ra}$	1600 y	(α)
$^{131}_{53}\mathrm{I}$	8.040 d	(β^-)	$^{228}_{88}\mathrm{Ra}$	5.75 y	(β^-)
$^{142}_{58}\mathrm{Ce}$	5×10^{15} y	(α)	$^{228}_{89}\mathrm{Ac}$	6.13 h	(β^-)
$^{208}_{81}\mathrm{Tl}$	3.07 m	(β^-)	$^{228}_{90}\mathrm{Th}$	1.913 y	(α)
$^{210}_{82}\mathrm{Pb}$	22.3 y	(β^-)	$^{232}_{90}\mathrm{Th}$	1.4×10^{10} y	(α)
$^{212}_{82}\mathrm{Pb}$	10.6 h	(β^-)	$^{233}_{90}\mathrm{Th}$	22 m	(β^-)
$^{214}_{82}\mathrm{Pb}$	26.8 m	(β^-)	$^{234}_{90}\mathrm{Th}$	24.10 d	(β^-)
$^{206}_{83}\mathrm{Bi}$	6.243 d	$(E.C.)$	$^{233}_{91}\mathrm{Pa}$	27 d	(β^-)
$^{233}_{92}\mathrm{U}$	1.59×10^{5} y	(α)	$^{242}_{96}\mathrm{Cm}$	162.8 d	(α)
$^{234}_{92}\mathrm{U}$	2.45×10^{5} y	(α)	$^{243}_{97}\mathrm{Bk}$	4.5 h	$(\alpha \text{ or } E.C.)$
$^{235}_{92}\mathrm{U}$	7.03×10^{8} y	(α)	$^{253}_{99}\mathrm{Es}$	20.47 d	(α)
$^{238}_{92}\mathrm{U}$	4.47×10^{9} y	(α)	$^{254}_{100}\mathrm{Fm}$	3.24 h	$(\alpha \text{ or } S.F.)$
$^{239}_{92}\mathrm{U}$	23.54 m	(β^-)	$^{255}_{100}\mathrm{Fm}$	20.1 h	(α)
$^{239}_{93}\mathrm{Np}$	2.3 d	(β^-)	$^{256}_{101}\mathrm{Md}$	76 m	$(\alpha \text{ or } E.C.)$
$^{239}_{94}\mathrm{Pu}$	2.407×10^{4} y	(α)	$^{254}_{102}\mathrm{No}$	55 s	(α)
$^{239}_{94}\mathrm{Pu}$	6.54×10^{3} y	(α)	$^{257}_{103}\mathrm{Lr}$	0.65 s	(α)
$^{241}_{94}\mathrm{Pu}$	14.4 y	$(\alpha \text{ or } \beta^-)$	$^{260}_{105}\mathrm{Ha}$	1.5 s	$(\alpha \text{ or } S.F.)$
$^{241}_{95}\mathrm{Am}$	432.2 y	(α)	$^{263}_{106}\mathrm{Sg}$	0.8 s	$(\alpha \text{ or } S.F.)$

Table M1

Footnotes

- 1y = years, d = days, h = hours, m = minutes, s = seconds
- 2*E.C.* = electron capture, *S.F.* = Spontaneous fission
- 3y = years, d = days, h = hours, m = minutes, s = seconds
- 4*E.C.* = electron capture, *S.F.* = Spontaneous fission

10.13: Appendix M- Half-Lives for Several Radioactive Isotopes is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

10.14: Answer Keys

10.14.1: Chapter 1 - Radioactivity and Nuclear Chemistry

10.14.2: Chapter 2 - Chemical Bonding and Molecular Geometry

10.14.3: Chapter 3 - Advanced Theories of Covalent Bonding

10.14.4: Chapter 4 - Thermochemistry

10.14.5: Chapter 5 - Thermodynamics

10.14.6: Chapter 6 - Fundamental Equilibrium Concepts

10.14.7: Chapter 7 - Acid-Base Equilibria

10.14.8: Chapter 8 - Kinetics

10.14.9: Chapter 9 - Electrochemistry

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

10.14.1: Chapter 1 - Radioactivity and Nuclear Chemistry

1.

(a) sodium-24; (b) aluminum-29; (c) krypton-73; (d) iridium-194

3.

(a) $^{34}_{14}\text{Si}$; (b) $^{36}_{15}\text{P}$; (c) $^{57}_{25}\text{Mn}$; (d) $^{121}_{56}\text{Ba}$

5.

(a) $^{45}_{25}\text{Mn}^{+1}$; (b) $^{69}_{45}\text{Rh}^{+2}$; (c) $^{142}_{53}\text{I}^{-1}$; (d) $^{243}_{97}\text{Bk}$

7.

Nuclear reactions usually change one type of nucleus into another; chemical changes rearrange atoms. Nuclear reactions involve much larger energies than chemical reactions and have measureable mass changes.

9.

(a), (b), (c), (d), and (e)

11.

(a) A nucleon is any particle contained in the nucleus of the atom, so it can refer to protons and neutrons. (b) An α particle is one product of natural radioactivity and is the nucleus of a helium atom. (c) A β particle is a product of natural radioactivity and is a high-speed electron. (d) A positron is a particle with the same mass as an electron but with a positive charge. (e) Gamma rays compose electromagnetic radiation of high energy and short wavelength. (f) Nuclide is a term used when referring to a single type of nucleus. (g) The mass number is the sum of the number of protons and the number of neutrons in an element. (h) The atomic number is the number of protons in the nucleus of an element.

13.

(a) $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow ^{30}_{15}\text{P} + ^{1}_{0}\text{n}$; (b) $^{239}_{94}\text{Pu} + ^{4}_{2}\text{He} \longrightarrow ^{242}_{96}\text{Cm} + ^{1}_{0}\text{n}$; (c) $^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$; (d) $^{235}_{92}\text{U} \longrightarrow ^{96}_{37}\text{Rb} + ^{135}_{55}\text{Cs} + 4^{1}_{0}\text{n}$

15.

(a) $^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$; (b) $^{14}_{7}\text{C} + ^{1}_{0}\text{n} \longrightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$; (c) $^{232}_{90}\text{Th} + ^{1}_{0}\text{n} \longrightarrow ^{233}_{90}\text{Th}$; (d) $^{238}_{92}\text{U} + ^{2}_{1}\text{H} \longrightarrow ^{239}_{92}\text{U} + ^{1}_{1}\text{H}$

17.

(a) 148.8 MeV per atom; (b) 7.808 MeV/nucleon

19.

α (helium nuclei), β (electrons), β^+ (positrons), and η (neutrons) may be emitted from a radioactive element, all of which are particles; γ rays also may be emitted.

21.

(a) conversion of a neutron to a proton: $^{1}_{0}\text{n} \longrightarrow ^{1}_{1}\text{p} + ^{0}_{+1}\text{e}$; (b) conversion of a proton to a neutron; the positron has the same mass as an electron and the same magnitude of positive charge as the electron has negative charge; when the n:p ratio of a nucleus is too low, a proton is converted into a neutron with the emission of a positron: $^{1}_{1}\text{p} \longrightarrow ^{1}_{0}\text{n} + ^{0}_{+1}\text{e}$; (c) In a proton-rich nucleus, an inner atomic electron can be absorbed. In simplest form, this changes a proton into a neutron: $^{1}_{1}\text{p} + ^{0}_{-1}\text{e} \longrightarrow ^{1}_{0}\text{p}$

23.

The electron pulled into the nucleus was most likely found in the 1*s* orbital. As an electron falls from a higher energy level to replace it, the difference in the energy of the replacement electron in its two energy levels is given off as an X-ray.

25.

Manganese-51 is most likely to decay by positron emission. The n:p ratio for Cr-53 is $\frac{29}{24}$ = 1.21; for Mn-51, it is $\frac{26}{25}$ = 1.04; for Fe-59, it is $\frac{33}{26}$ = 1.27. Positron decay occurs when the n:p ratio is low. Mn-51 has the lowest n:p ratio and therefore is most likely to decay by positron emission. Besides, $^{53}_{24}\text{Cr}$ is a stable isotope, and $^{59}_{26}\text{Fe}$ decays by beta emission.

27.

(a) β decay; (b) α decay; (c) positron emission; (d) β decay; (e) α decay

29.

$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$; $^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e}$; $^{234}_{91}\text{Pa} \longrightarrow {}^{234}_{92}\text{U} + {}^{0}_{-1}\text{e}$; $^{234}_{92}\text{U} \longrightarrow {}^{230}_{90}\text{Th} + {}^{4}_{2}\text{He}$
$^{230}_{90}\text{Th} \longrightarrow {}^{226}_{88}\text{Ra} + {}^{4}_{2}\text{He}$ $^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$; $^{222}_{86}\text{Rn} \longrightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$

31.

Half-life is the time required for half the atoms in a sample to decay. Example (answers may vary): For C-14, the half-life is 5770 years. A 10-g sample of C-14 would contain 5 g of C-14 after 5770 years; a 0.20-g sample of C-14 would contain 0.10 g after 5770 years.

33.

$\left(\frac{1}{2}\right)^{0.04} = 0.973$ or 97.3%

35.

2×10^3 y

37.

0.12 h^{-1}

39.

(a) 3.8 billion years; (b) The rock would be younger than the age calculated in part (a). If Sr was originally in the rock, the amount produced by radioactive decay would equal the present amount minus the initial amount. As this amount would be smaller than the amount used to calculate the age of the rock and the age is proportional to the amount of Sr, the rock would be younger.

41.

c = 0; This shows that no Pu-239 could remain since the formation of the earth. Consequently, the plutonium now present could not have been formed with the uranium.

43.

17.5 MeV

45.

(a) $^{212}_{83}\text{Bi} \longrightarrow {}^{212}_{84}\text{Po} + {}^{0}_{-1}\text{e}$; (b) $^{8}_{5}\text{B} \longrightarrow {}^{8}_{4}\text{Be} + {}^{0}_{-1}\text{e}$; (c) $^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{Np}$, $^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e}$; (d) $^{90}_{38}\text{Sr} \longrightarrow {}^{90}_{39}\text{Y} + {}^{0}_{-1}\text{e}$

47.

(a) $^{241}_{95}\text{Am} + {}^{4}_{2}\text{He} \longrightarrow {}^{244}_{97}\text{Bk} + {}^{1}_{0}\text{n}$; (b) $^{239}_{94}\text{Pu} + 15\,{}^{1}_{0}\text{n} \longrightarrow {}^{254}_{100}\text{Fm} + 6\,{}^{0}_{-1}\text{e}$; (c) $^{250}_{98}\text{Cf} + {}^{11}_{5}\text{B} \longrightarrow {}^{257}_{103}\text{Lr} + 4\,{}^{1}_{0}\text{n}$; (d) $^{249}_{98}\text{Cf} + {}^{15}_{7}\text{N} \longrightarrow {}^{260}_{105}\text{Db} + 4\,{}^{1}_{0}\text{n}$

49.

Two nuclei must collide for fusion to occur. High temperatures are required to give the nuclei enough kinetic energy to overcome the very strong repulsion resulting from their positive charges.

51.

A nuclear reactor consists of the following:

1. A nuclear fuel. A fissionable isotope must be present in large enough quantities to sustain a controlled chain reaction. The radioactive isotope is contained in tubes called fuel rods.
2. A moderator. A moderator slows neutrons produced by nuclear reactions so that they can be absorbed by the fuel and cause additional nuclear reactions.
3. A coolant. The coolant carries heat from the fission reaction to an external boiler and turbine where it is transformed into electricity.
4. A control system. The control system consists of control rods placed between fuel rods to absorb neutrons and is used to adjust the number of neutrons and keep the rate of the chain reaction at a safe level.
5. A shield and containment system. The function of this component is to protect workers from radiation produced by the nuclear reactions and to withstand the high pressures resulting from high-temperature reactions.

53.

The fission of uranium generates heat, which is carried to an external steam generator (boiler). The resulting steam turns a turbine that powers an electrical generator.

55.

Introduction of either radioactive Ag^+ or radioactive Cl^- into the solution containing the stated reaction, with subsequent time given for equilibration, will produce a radioactive precipitate that was originally devoid of radiation.

57.

(a) ${}^{133}_{53}\text{I} \longrightarrow {}^{133}_{54}\text{Xe} + {}^{0}_{-1}\text{e}$; (b) 37.6 days

59.

Alpha particles can be stopped by very thin shielding but have much stronger ionizing potential than beta particles, X-rays, and γ-rays. When inhaled, there is no protective skin covering the cells of the lungs, making it possible to damage the DNA in those cells and cause cancer.

61.

(a) 7.64×10^9 Bq; (b) 2.06×10^{-2} Ci

10.14.1: Chapter 1 - Radioactivity and Nuclear Chemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

10.14.2: Chapter 2 - Chemical Bonding and Molecular Geometry

1.

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

3.

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

5.

(a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}

7.

(a) $[Ar]4s^2 3d^{10} 4p^6$; (b) $[Kr]4d^{10} 5s^2 5p^6$ (c) $1s^2$ (d) $[Kr]4d^{10}$; (e) $[He]2s^2 2p^6$; (f) $[Ar]3d^{10}$; (g) $1s^2$ (h) $[He]2s^2 2p^6$ (i) $[Kr]4d^{10} 5s^2$ (j) $[Ar]3d^7$ (k) $[Ar]3d^6$, (l) $[Ar]3d^{10} 4s^2$

9.

(a) $1s^2 2s^2 2p^6 3s^2 3p^1$; Al^{3+}: $1s^2 2s^2 2p^6$; (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$; Sr^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (d) $1s^2 2s^1$; Li^{+}: $1s^2$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (f) $1s^2 2s^2 2p^6 3s^2 3p^4$; $1s^2 2s^2 2p^6 3s^2 3p^6$

11.

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

13.

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

15.

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

17.

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

19.

N, O, F, and Cl

21.

(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

23.

(a) eight electrons:



(b) eight electrons:



(c) no electrons Be^{2+}
(d) eight electrons:



(e) no electrons Ga^{3+}
(f) no electrons Li^{+}
(g) eight electrons:



25.

(a)



(b)



(c)



(d)



(e)



(f)

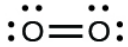


27.



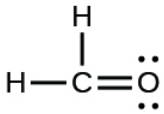
29.

(a)

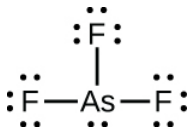


In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

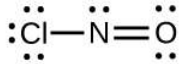
(b)



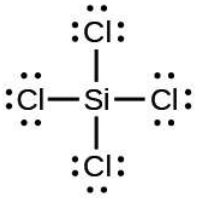
(c)



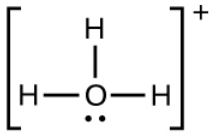
(d)



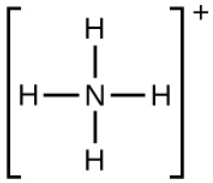
(e)



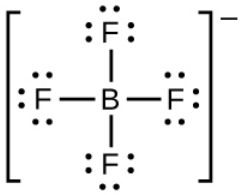
(f)



(g)



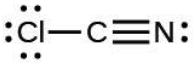
(h)



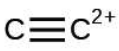
(i)



(j)

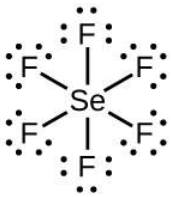


(k)

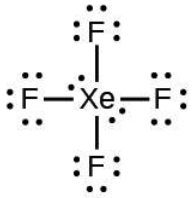


31.

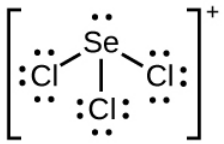
(a) SeF_6:



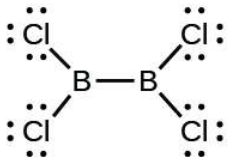
(b) XeF_4:



(c)



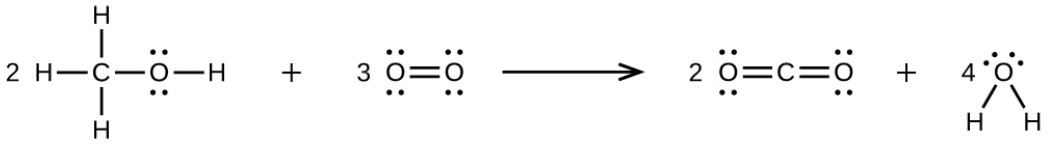
(d) Cl_2BBCl_2:

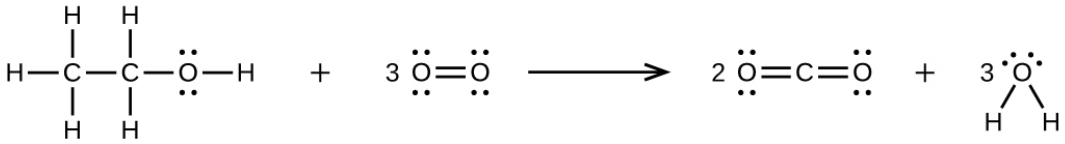


33.

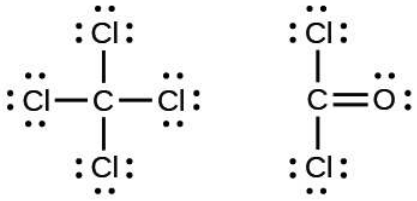
Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

35.



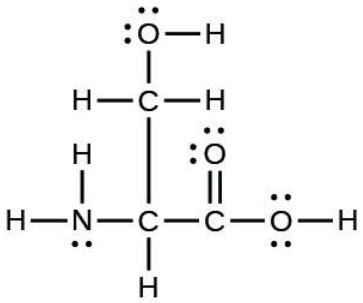


37.

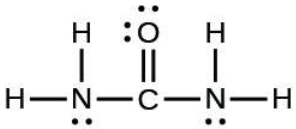


39.

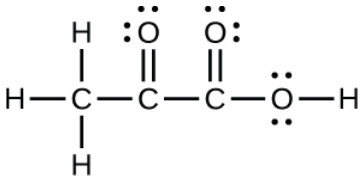
(a)



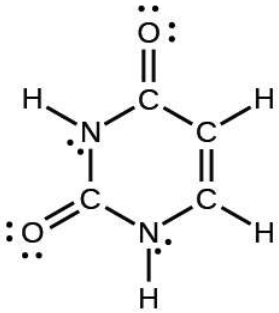
(b)



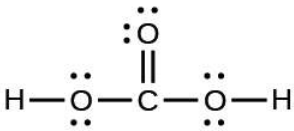
(c)



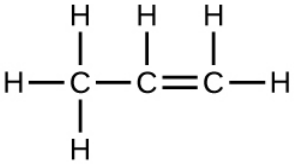
(d)



(e)



41.

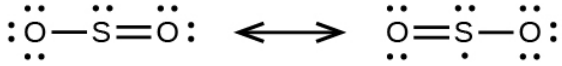


43.

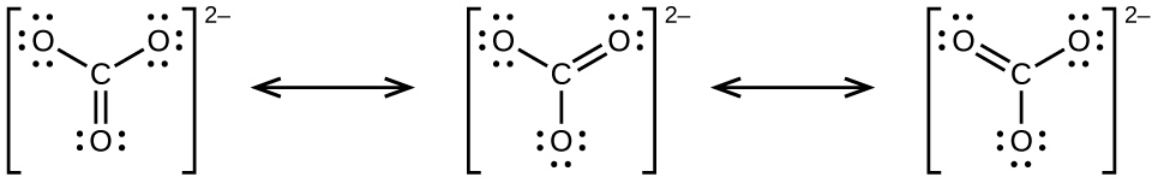
Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

45.

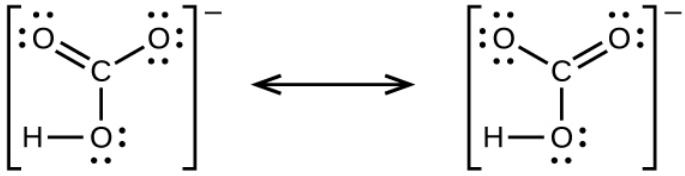
(a)



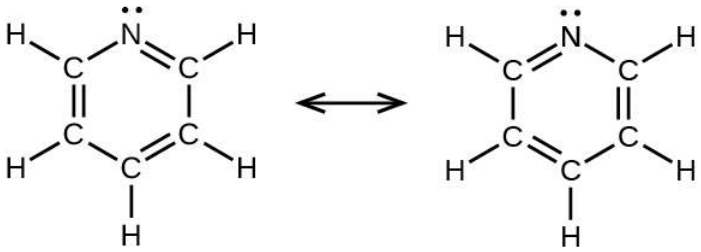
(b)



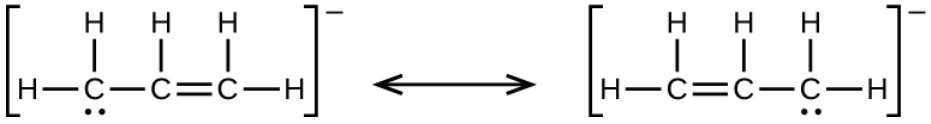
(c)



(d)

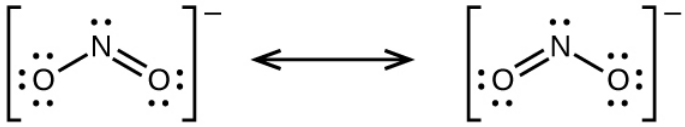


(e)



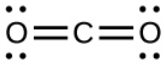
47.

For NO_2^-



49.

(a)



(b)



CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

51.

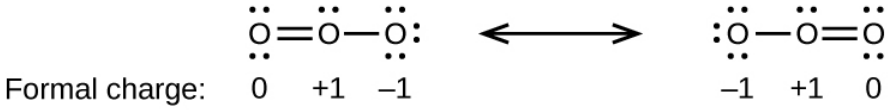
(a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl 0; (d) P: 0, F: 0

53.

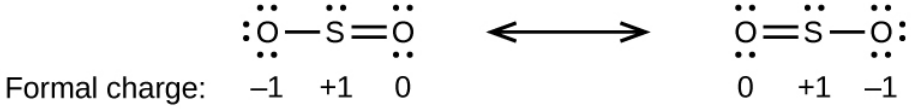
Cl in Cl_2: 0; Cl in $BeCl_2$: 0; Cl in ClF_5: 0

55.

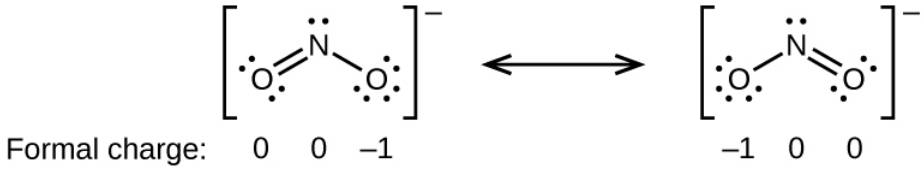
(a)



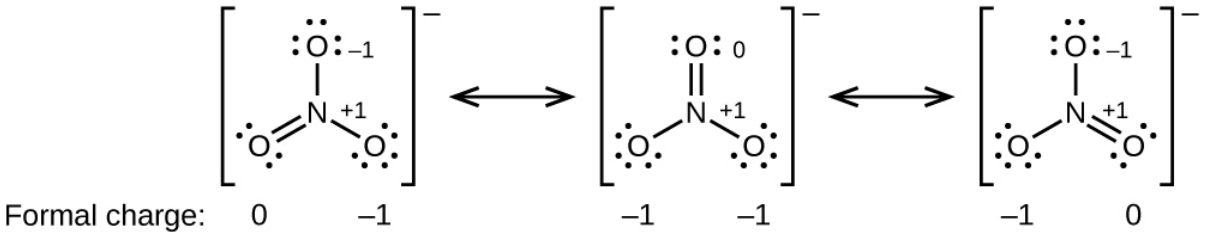
(b)



(c)



(d)

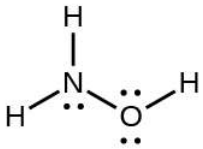


57.

HOCl

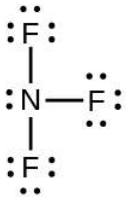
59.

The structure that gives zero formal charges is consistent with the actual structure:

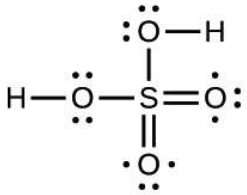


61.

NF_3;



63.



65.

(a) −114 kJ; (b) 30 kJ; (c) −1055 kJ

67.

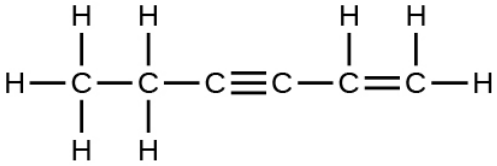
The greater bond energy is in the figure on the left. It is the more stable form.

69.

71.

The S–F bond in SF_4 is stronger.

73.



The C–C single bonds are longest.

75.

(a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower $n = 3$ level, which is much smaller in radius. (b) The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion. (c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level. (d) In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

77.

(d)

79.

4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

81.

(a) Na_2O; Na^+ has a smaller radius than K^+; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

83.

(e)

85.

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

87.

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

89.

As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

91.

(a) Both the electron geometry and the molecular structure are octahedral. (b) Both the electron geometry and the molecular structure are trigonal bipyramid. (c) Both the electron geometry and the molecular structure are linear. (d) Both the electron geometry and the molecular structure are trigonal planar.

93.

(a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

95.

(a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

97.

All of these molecules and ions contain polar bonds. Only ClF_5, PCl_3, SeF_4, and have dipole moments.

99.

SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

101.

P

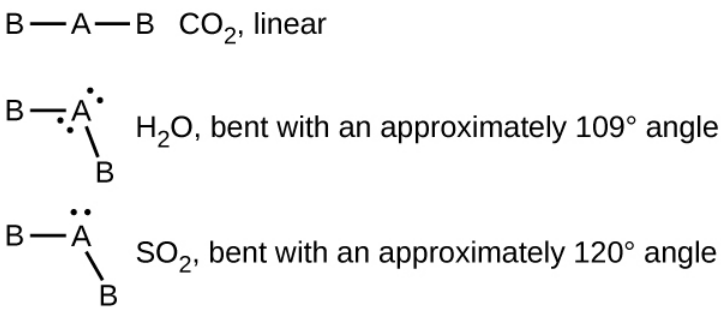
103.

nonpolar

105.

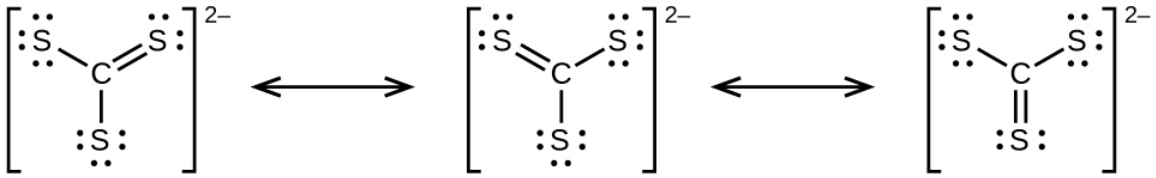
(a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) $\underline{C}H_3CCH$ tetrahedral, $CH_3\underline{C}\underline{C}H$ linear; (h) tetrahedral; (i) $H_2C\underline{C}CH_2$ linear; $H_2\underline{C}C\underline{C}H_2$ trigonal planar

107.

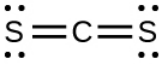


109.

(a)



(b)



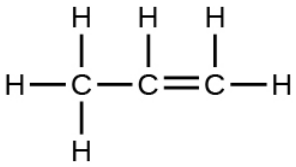
(c)



(d) includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

111.

The Lewis structure is made from three units, but the atoms must be rearranged:



113.

The molecular dipole points away from the hydrogen atoms.

115.

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

10.14.2: Chapter 2 - Chemical Bonding and Molecular Geometry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 7** is licensed CC BY 4.0.

10.14.3: Chapter 3 - Advanced Theories of Covalent Bonding

1.

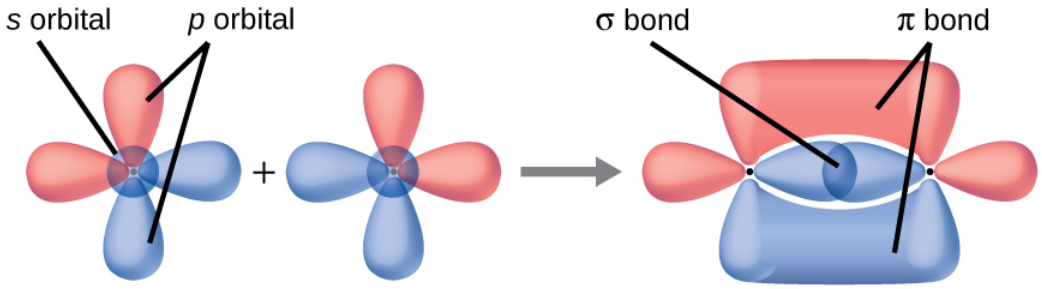
Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. Differences: σ bonds are stronger and result from end-to-end overlap and all single bonds are σ bonds; π bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more π bonds (in addition to a σ bond).

3.

The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

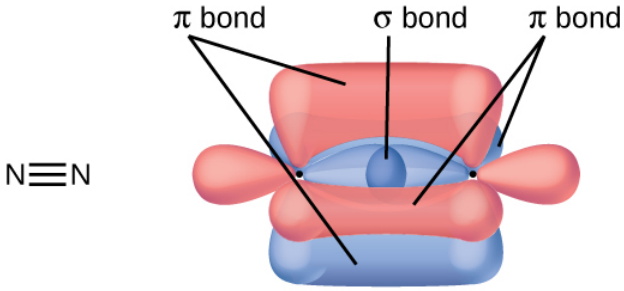
5.

Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side-by-side to form the π bond.



7.

No, two of the *p* orbitals (one on each N) will be oriented end-to-end and will form a σ bond.



9.

Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.

11.

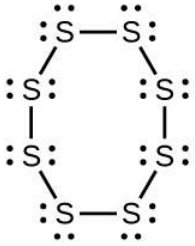
There are no *d* orbitals in the valence shell of carbon.

13.

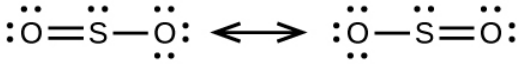
trigonal planar, sp^2; trigonal pyramidal (one lone pair on A) sp^3; T-shaped (two lone pairs on A sp^3d, or (three lone pairs on A) sp^3d^2

15.

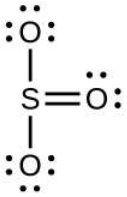
(a) Each S has a bent (109°) geometry, sp^3



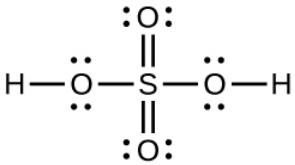
(b) Bent (120°), sp^2



(c) Trigonal planar, sp^2



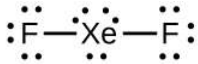
(d) Tetrahedral, sp^3



17.

(a) XeF_2

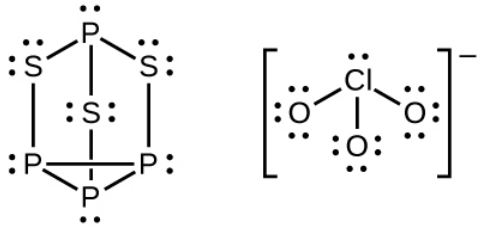
(b)



(c) linear (d) sp^3d

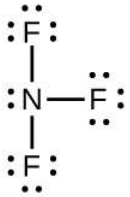
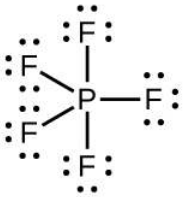
19.

(a)



(b) P atoms, trigonal pyramidal; S atoms, bent, with two lone pairs; Cl atoms, trigonal pyramidal; (c) Hybridization about P, S, and Cl is, in all cases, sp^3; (d) Oxidation states P +1, S Cl +5, O –2. Formal charges: P 0; S 0; Cl +2: O –1

21.

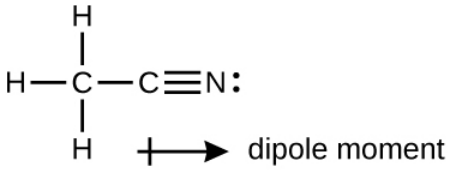
Phosphorus and nitrogen can form sp^3 hybrids to form three bonds and hold one lone pair in PF_3 and NF_3, respectively. However, nitrogen has no valence *d* orbitals, so it cannot form a set of sp^3d hybrid orbitals to bind five fluorine atoms in NF_5. Phosphorus has *d* orbitals and can bind five fluorine atoms with sp^3d hybrid orbitals in PF_5.

23.

A triple bond consists of one σ bond and two π bonds. A σ bond is stronger than a π bond due to greater overlap.

25.

(a)



(b) The terminal carbon atom uses sp^3 hybrid orbitals, while the central carbon atom is *sp* hybridized. (c) Each of the two π bonds is formed by overlap of a 2*p* orbital on carbon and a nitrogen 2*p* orbital.

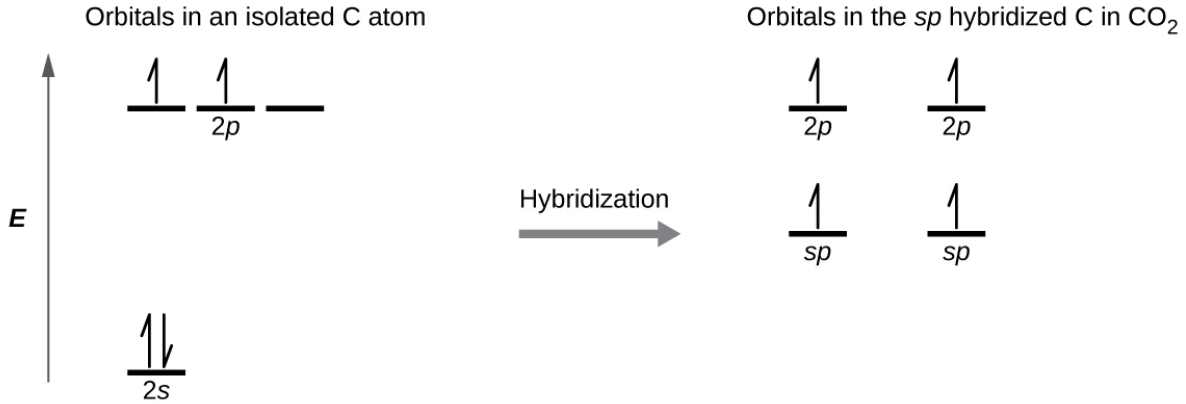
27.

(a) sp^2; (b) *sp*; (c) sp^2; (d) sp^3; (e) sp^3; (f) sp^3d; (g) sp^3

29.

(a) sp^2, delocalized; (b) *sp*, localized; (c) sp^2, delocalized; (d) sp^3, delocalized

31.



Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

33.

(a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons. Differences: σ orbitals are end-to-end combinations of atomic orbitals, whereas π orbitals are formed by side-by-side overlap of orbitals. (b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule. Differences: ψ for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule, ψ represents a mathematical combination of atomic orbitals. (c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

35.

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

37.

Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding positively charged nuclei and negatively charged electrons stabilizes the system.

39.

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

41.

(a) H_2 bond order = 1, bond order = 0.5, bond order = 0.5, strongest bond is H_2; (b) O_2 bond order = 2, bond order = 3; bond order = 1, strongest bond is (c) Li_2 bond order = 1, bond order = 0.5, Be_2 bond order = 0, strongest bond is ;(d) F_2 bond order = 1, bond order = 1.5, bond order = 0.5, strongest bond is (e) N_2 bond order = 3, bond order = 2.5, bond order = 2.5, strongest bond is N_2

43.

(a) H_2; (b) N_2; (c) O; (d) C_2; (e) B_2

45.

Yes, fluorine is a smaller atom than Li, so atoms in the 2*s* orbital are closer to the nucleus and more stable.

47.

2+

49.

N_2 has s-p mixing, so the π orbitals are the last filled in O_2 does not have s-p mixing, so the σ_p orbital fills before the π orbitals.

10.14.3: Chapter 3 - Advanced Theories of Covalent Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 8** is licensed CC BY 4.0.

10.14.4: Chapter 4 - Thermochemistry

1.

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

3.

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

5.

(a) 47.6 J/°C; 11.38 cal $°C^{-1}$; (b) 407 J/°C; 97.3 cal $°C^{-1}$

7.

1310 J; 313 cal

9.

7.15 °C

11.

(a) 0.390 J/g °C; (b) Copper is a likely candidate.

13.

We assume that the density of water is 1.0 g/cm^3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. Energy required = 7.47 kWh

15.

lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

17.

greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings": $q_{rxn} = -(q_{solution} + q_{calorimeter})$; since both $q_{solution}$ and $q_{calorimeter}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

19.

The temperature of the coffee will drop 1 degree.

21.

5.7 10^2 kJ

23.

38.5 °C

25.

−2.2 kJ; The heat produced shows that the reaction is exothermic.

27.

1.4 kJ

29.

22.6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

31.

11.7 kJ

33.

30%

35.

0.24 g

37.

1.4 10^2 Calories

39.

The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0.0500 mol HCl and 0.0500 mol NaOH.

41.

25 kJ mol^{-1}

43.

81 kJ mol^{-1}

45.

5204.4 kJ

47.

1.83 10^{-2} mol

49.

–802 kJ mol^{-1}

51.

15.5 kJ/ºC

53.

7.43 g

55.

Yes.

57.

459.6 kJ

59.

−494 kJ/mol

61.

44.01 kJ/mol

63.

−394 kJ

65.

265 kJ

67.

90.3 kJ/mol

69.

(a) −1615.0 kJ mol^{-1}; (b) −484.3 kJ mol^{-1}; (c) 164.2 kJ; (d) −232.1 kJ

71.

−54.04 kJ mol^{-1}

73.

−2660 kJ mol^{-1}

75.

–66.4 kJ

77.

−122.8 kJ

79.

3.7 kg

81.

On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.

83.

−88.2 kJ

85.

(a) (b) 1570 L air; (c) −104.5 kJ mol^{-1}; (d) 75.4 °C

10.14.4: Chapter 4 - Thermochemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 5** is licensed CC BY 4.0.

10.14.5: Chapter 5 - Thermodynamics

1.

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

3.

(a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

5.

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

13.

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

15.

(a) $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) $C_2H_5OH(g)$ as it is in the gaseous state. (c) $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

17.

(a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

19.

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

21.

(a) 107 J/K; (b) −86.4 J/K; (c) 133.2 J/K; (d) 118.8 J/K; (e) −326.6 J/K; (f) −171.9 J/K; (g) −7.2 J/K

23.

100.6 J/K

25.

(a) −198.1 J/K; (b) −348.9 J/K

27.

As $\Delta S_{univ} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

29.

(a) 2.86 J/K; (b) 24.8 J/K; (c) −113.2 J/K; (d) −24.7 J/K; (e) 15.5 J/K; (f) 290.0 J/K

31.

The reaction is nonspontaneous at room temperature.
Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

33.

(a) 465.1 kJ nonspontaneous; (b) −106.86 kJ spontaneous; (c) −291.9 kJ spontaneous; (d) −83.4 kJ spontaneous; (e) −406.7 kJ spontaneous; (f) −154.3 kJ spontaneous

35.

(a) The standard free energy of formation is –1124.3 kJ/mol. (b) The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

37.

(a) The reaction is nonspontaneous; (b) Above 566 °C the process is spontaneous.

43.

(a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; (b) K_p = 0.031; (c) The evaporation of water is spontaneous; (d) must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

45.

(a) Nonspontaneous as (b) The forward reaction to produce F6P is spontaneous under these conditions.

47.

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

49.

(a) Increasing the oxygen partial pressure will yield a decrease in Q and thus becomes more negative. (b) Increasing the oxygen partial pressure will yield a decrease in Q and thus becomes more negative. (c) Increasing the oxygen partial pressure will yield an increase in Q and thus becomes more positive.

10.14.5: Chapter 5 - Thermodynamics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 16** is licensed CC BY 4.0.

10.14.6: Chapter 6 - Fundamental Equilibrium Concepts

1.

The reaction can proceed in both the forward and reverse directions.

3.

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the forward and reverse reactions continue to proceed, but at equal rates.

5.

Not necessarily. A system at equilibrium is characterized by *constant* reactant and product concentrations, but the values of the reactant and product concentrations themselves need not be equal.

7.

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

9.

(a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) > 1 because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

11.

Since a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

13.

$K_c > 1$

15.

(a) (b) (c) (d) $Q_c = [SO_2]$; (e) (f) (g) (h) $Q_c = [H_2O]^5$

17.

(a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

19.

The system will shift toward the reactants to reach equilibrium.

21.

(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

23.

This situation occurs in (a) and (b).

25.

(a) $K_P = 1.6\ 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.34\ 10^{-39}$; (d) $K_c = 4.60\ 10^{-3}$

31.

The amount of $CaCO_3$ must be so small that is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full required for equilibrium.

33.

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the

reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

34.

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

36.

Add N_2; add H_2; decrease the container volume; heat the mixture.

38.

(a) *T* increase = shift right, *V* decrease = shift left; (b) *T* increase = shift right, *V* = no effect; (c) *T* increase = shift left, *V* decrease = shift left; (d) *T* increase = shift left, *V* decrease = shift right.

40.

(a) (b) [H_2] increases, [CO] decreases, [CH_3OH] increases; (c), [H_2] increases, [CO] decreases, [CH_3OH] decreases; (d), [H_2] increases, [CO] increases, [CH_3OH] increases; (e), [H_2] increases, [CO] increases, [CH_3OH] decreases; (f), no changes.

42.

(a) (b) [H_2O] no change, [CO] no change, [H_2] no change; (c) [H_2O] decreases, [CO] decreases, [H_2] decreases; (d) [H_2O] increases, [CO] increases, [H_2] decreases; (e) [H_2O] decreases, [CO] increases, [H_2] increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

44.

Only (b)

46.

Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(*s*).

48.

Though the solution is saturated, the dynamic nature of the solubility equilibrium means the opposing processes of solid dissolution and precipitation continue to occur (just at equal rates, meaning the dissolved ion concentrations and the amount of undissolved solid remain constant). The radioactive Ag^+ ions detected in the solution phase come from dissolution of the added solid, and their presence is countered by precipitation of nonradioactive Ag^+.

50.

[A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

52.

$K_c = 6.00\ 10^{-2}$

54.

$K_c = 0.50$

56.

$K_P = 1.9\ 10^3$

58.

$K_P = 3.06$

60.

(a) $-2x$, $+2x$; (b) , , $-2x$; (c) $-2x$, $3x$; (d) x, $-x$, $-3x$; (e) $+x$; (f)

62.

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

64.

$[NH_3] = 9.1\ 10^{-2}\ M$

66.

$P_{BrCl} = 4.9\ 10^{-2}$ atm

68.

$[CO] = 2.04\ 10^{-4}\ M$

70.

72.

Calculate Q based on the calculated concentrations and see if it is equal to K_c. Because Q does equal 4.32, the system must be at equilibrium.

74.

(a) $[NO_2] = 1.17\ 10^{-3}\ M$; $[N_2O_4] = 0.128\ M$; (b) The assumption that x is negligibly small compared to 0.129 is confirmed by comparing the initial concentration of the N_2O_4 to its concentration at equilibrium (they differ by just 1 in the least significant digit's place).

76.

(a) $[H_2S] = 0.810$ atm, $[H_2] = 0.014$ atm, $[S_2] = 0.0072$ atm; (b) The assumption that $2x$ is negligibly small compared to 0.824 is confirmed by comparing the initial concentration of the H_2S to its concentration at equilibrium (0.824 atm versus 0.810 atm, a difference of less than 2%).

78.

$[PCl_5] = 1.80\ M$; $[Cl_2] = 0.195\ M$; $[PCl_3] = 0.195\ M$.

79.

507 g

81.

330 g

84.

(a) 0.33 mol. (b) $[CO_2] = 0.50\ M$. Added H_2 forms some water as a result of a shift to the left after H_2 is added.

86.

(a) (b) $[NH_3]$ must increase for Q_c to reach K_c. (c) The increase in system volume would lower the partial pressures of all reactants (including NO_2). (d)

103.

(a) $1.5\ 10^2$ kJ; (b) −21.9 kJ; (c) −5.34 kJ; (d) −0.383 kJ; (e) 18 kJ; (f) 71 kJ

105.

(a) $K = 41$; (b) $K = 0.053$; (c) $K = 6.9\ 10^{13}$; (d) $K = 1.9$; (e) $K = 0.04$

10.14.6: Chapter 6 - Fundamental Equilibrium Concepts is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 13** is licensed CC BY 4.0.

10.14.7: Chapter 7 - Acid-Base Equilibria

1.

One example for NH_3 as a conjugate acid: as a conjugate base:

3.

(a) (b) (c) (d) (e) (f)

5.

(a) (b) (c) (d) (e) (f)

7.

(a) H_2O, O^{2-}; (b) H_3O^+, OH^-; (c) H_2CO_3, (d) (e) H_2SO_4, (f) (g) H_2S; S^{2-}; (h) H_4N_2

9.

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) HNO_3(BA), H_2O(BB), H_3O^+(CA), (b) CN^-(BB), H_2O(BA), HCN(CA), OH^-(CB); (c) H_2SO_4(BA), Cl^-(BB), HCl(CA), (d) OH^-(BB), (CB), H_2O(CA); (e) O^{2-}(BB), H_2O(BA) OH^-(CB and CA); (f) $[Cu(H_2O)_3(OH)]^+$(BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); (g) H_2S(BA), HS^-(CB), NH_3(CA)

11.

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O. As an acid: As a base:

13.

amphiprotic: (a) (b) not amphiprotic: (c) Br^-; (d) (e)

15.

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C, $[H_3O^+] = [OH^-] = (2.910 \times 10^{-14})^{1/2} = 1.7\ 10^{-7}$.

17.

$x = 3.051\ 10^{-7}\ M = [H_3O^+] = [OH^-]$; pH = $-\log 3.051\ 10^{-7} = -(-6.5156) = 6.5156$; pOH = pH = 6.5156

19.

(a) pH = 3.587; pOH = 10.413; (b) pOH = 0.68; pH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pOH = −0.40; pH = 14.4

21.

$[H_3O^+] = 3.0\ 10^{-7}\ M$; $[OH^-] = 3.3\ 10^{-8}\ M$

23.

$[H_3O^+] = 1\ 10^{-2}\ M$; $[OH^-] = 1\ 10^{-12}\ M$

25.

$[OH^-] = 3.1\ 10^{-12}\ M$

27.

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

29.

$[H_2O] > [CH_3CO_2H] > \approx > [OH^-]$

31.

The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

33.

35.

37.

The stronger base or stronger acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and

39.

triethylamine

41.

(a) higher electronegativity of the central ion. (b) H_2O; NH_3 is a base and water is neutral, or decide on the basis of K_a values. (c) HI; PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI. (d) PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e) HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

43.

(a) $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b) the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c) HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d) $HOCl < HOClO < HOClO_2 < HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e) and are anions of weak bases, so they act as strong bases toward H^+. and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f) with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

45.

47.

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

48.

(b) The addition of HCl

50.

(a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of ions and decreasing the concentration of OH^- ions. (c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of ions and decreasing the concentrations of HNO_2. (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding KNO_2 adds ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

52.

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

54.

(a) (b) (c) (d)

56.

58.

(a) (b) (c) (d) (e) (f)

60.

(a)

Solving for x gives 1.63 10^{-5} M. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [ClO^-] = 1.6\ 10^{-5}\ M$

$[HClO^-] = 0.0092\ M$

$[OH^-] = 6.1\ 10^{-10}\ M$;

(b)

Solving for x gives 5.81 10^{-6} M. This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$= [OH^-] = 5.8\ 10^{-6}\ M$

$[C_6H_5NH_2] = 0.0784\ M$

$[H_3O^+] = 1.7\ 10^{-9}\ M$;

(c)

Solving for x gives 6.30 10^{-6} M. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [CN^-] = 6.3\ 10^{-6}\ M$

$[HCN] = 0.0810\ M$

$[OH^-] = 1.6\ 10^{-9}\ M$;

(d)

Solving for x gives 2.63 10^{-3} M. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[(CH_3)_3NH^+] = [OH^-] = 2.6\ 10^{-3}\ M$

$[(CH_3)_3N] = 0.11\ M$

$[H_3O^+] = 3.8\ 10^{-12}\ M$;

(e)

Solving for x gives 1.39 10^{-4} M. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4\ 10^{-4}\ M$

$= 0.120\ M$

$[OH^-] = 7.2\ 10^{-11}\ M$

62.

pH = 2.41

64.

$[C_{10}H_{14}N_2] = 0.049\ M$; $[C_{10}H_{14}N_2H^+] = 1.9\ 10^{-4}\ M$; $= 1.4\ 10^{-11}\ M$; $[OH^-] = 1.9\ 10^{-4}\ M$; $[H_3O^+] = 5.3\ 10^{-11}\ M$

66.

68.

70.

(a) acidic; (b) basic; (c) acidic; (d) neutral

72.

$[H_3O^+]$ and are practically equal

74.

$[C_6H_4(CO_2H)_2]$ 7.2 10^{-3} M, $[C_6H_4(CO_2H)(CO_2)^-] = [H_3O^+]$ 2.8 10^{-3} M, 3.9 10^{-6} M, $[OH^-]$ 3.6 10^{-12} M

76.

(a)

(b)

(c)

Solving for x gives 1.5 10^{-11} M. Therefore, compared with 0.014 M, this value is negligible (1.1 10^{-7}%).

78.

Excess H_3O^+ is removed primarily by the reaction:
Excess base is removed by the reaction:

80.

$[H_3O^+] = 1.5\ 10^{-4}\ M$

82.

$[OH^-] = 4.2\ 10^{-4}\ M$

84.

(a) The added HCl will increase the concentration of H_3O^+ slightly, which will react with and produce CH_3CO_2H in the process. Thus, decreases and $[CH_3CO_2H]$ increases. (b) The added KCH_3CO_2 will increase the concentration of which will react with H_3O^+ and produce CH_3CO_2 H in the process. Thus, $[H_3O^+]$ decreases slightly and $[CH_3CO_2H]$ increases. (c) The added NaCl will have no effect on the concentration of the ions. (d) The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and increases. (e) The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and increases.

86.

pH = 8.95

88.

37 g (0.27 mol)

90.

(a) pH = 5.222; (b) The solution is acidic. (c) pH = 5.220

92.

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

94.

(a) pH = 2.50; (b) pH = 4.01; (c) pH = 5.60; (d) pH = 8.35; (e) pH = 11.08

10.14.7: Chapter 7 - Acid-Base Equilibria is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 14** is licensed CC BY 4.0.

10.14.8: Chapter 8 - Kinetics

1.

The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.

3.

5.

(a) average rate, 0 − 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 10 − 20 s = 0.0265 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.023 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.012 mol L^{-1} s^{-1}

7.

Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because more reactive surface exists.

9.

(a) Depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other. (b) Particles of reactant must come into contact with each other before they can react.

11.

(a) very slow; (b) As the temperature is increased, the reaction proceeds at a faster rate. The amount of reactants decreases, and the amount of products increases. After a while, there is a roughly equal amount of *BC*, *AB*, and *C* in the mixture and a slight excess of *A*.

13.

(a) 2; (b) 1

15.

(a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

17.

4.3 10^{-5} mol/L/s

19.

7.9 10^{-13} mol/L/year

21.

rate = k; k = 2.0 10^{-2} mol L^{-1} h^{-1} (about 0.9 g L^{-1} h^{-1} for the average male); The reaction is zero order.

23.

rate = $k[NOCl]^2$; k = 8.0 10^{-8} L/mol/h; second order

25.

rate = $k[NO]^2[Cl_2]$; k = 9.1 L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

27.

(a) The rate law is second order in A and is written as rate = $k[A]^2$. (b) k = 7.88 10^{-3} L mol^{-1} s^{-1}

29.

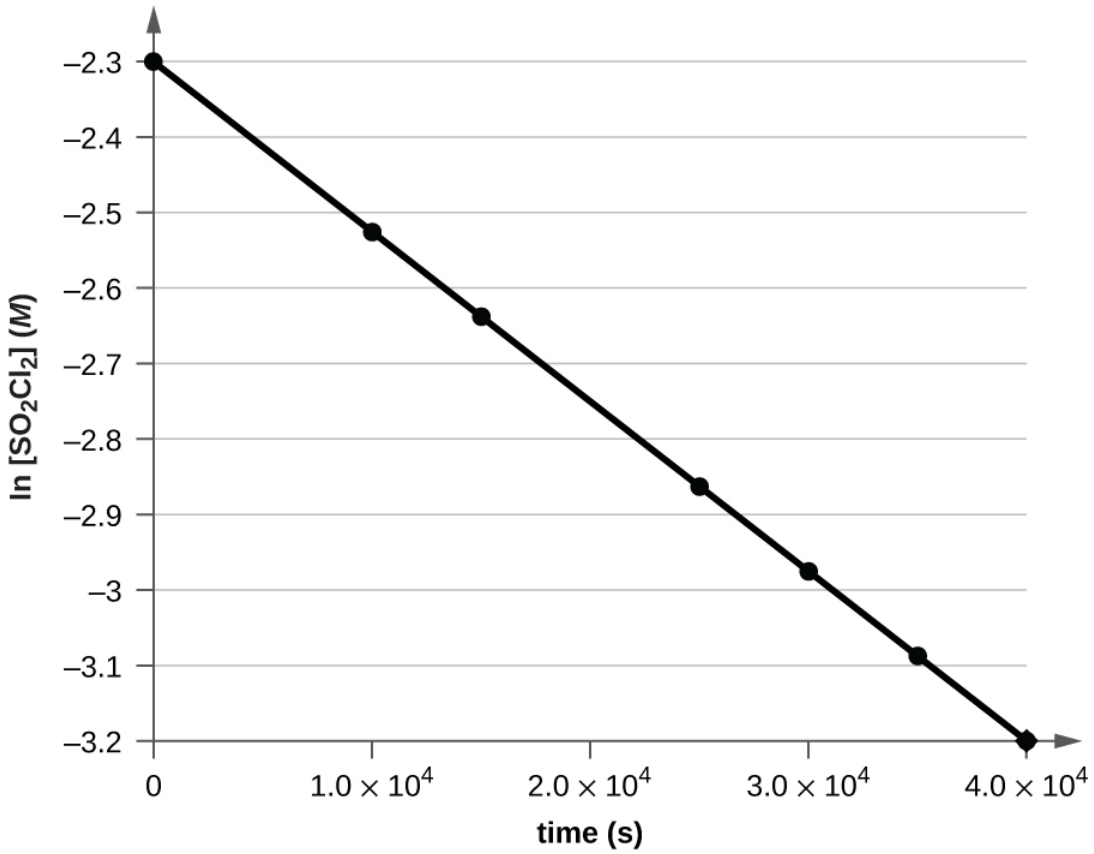
(a) 2.5 10^{-4} mol/L/min

31.

rate = $k[I^-][OCl^-]$; k = 6.1 10^{-2} L mol^{-1} s^{-1}

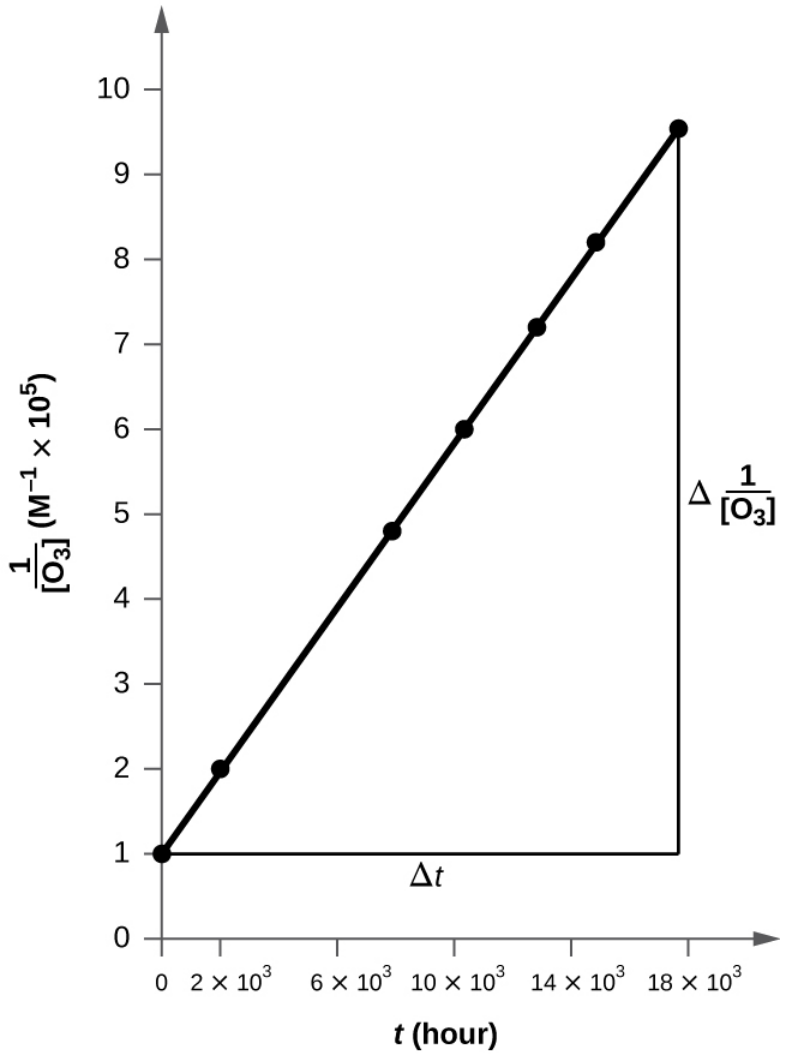
33.

Plotting a graph of $\ln[SO_2Cl_2]$ versus t reveals a linear trend; therefore we know this is a first-order reaction:



$k = 2.20\ 10^{-5}\ s^{-1}$

34.



The plot is nicely linear, so the reaction is second order. k = 50.1 L mol^{-1} h^{-1}

36.

14.3 d

38.

8.3 10^7 s

40.

0.826 s

42.

The reaction is first order. k = 1.0 10^7 L mol^{-1} min^{-1}

44.

1.16 × 10^3 s ; 20% remains

46.

252 days

48.

$[A]_0$ (M)	k 10^3 (s^{-1})

$[A]_0$ (M)	$k\ 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.53
1.81	2.58
5.33	2.36
4.05	2.47
2.95	2.48
1.72	2.43

50.

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

52.

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

54.

After finding k at several different temperatures, a plot of ln k versus gives a straight line with the slope from which E_a may be determined.

56.

(a) 4-times faster (b) 128-times faster

58.

60.

43.0 kJ/mol

62.

177 kJ/mol

64.

E_a = 108 kJ; A = 2.0 10^8 s^{-1}; k = 3.2 10^{-10} s^{-1}; (b) 1.81 10^8 h or 7.6 10^6 day; (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

66.

The A atom has enough energy to react with BC; however, the different angles at which it bounces off of BC without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

68.

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate law. Yes. If the reaction is an elementary reaction, then doubling the concentration of A doubles the rate.

70.

Rate = $k[A][B]^2$; Rate = $k[A]^3$

72.

(a) $Rate_1 = k[O_3]$; (b) $Rate_2 = k[O_3][Cl]$; (c) $Rate_3 = k[ClO][O]$; (d) $Rate_2 = k[O_3][NO]$; (e) $Rate_3 = k[NO_2][O]$

74.

(a) Doubling $[H_2]$ doubles the rate. $[H_2]$ must enter the rate law to the first power. Doubling [NO] increases the rate by a factor of 4. [NO] must enter the rate law to the second power. (b) Rate = $k\,[NO]^2[H_2]$; (c) $k = 5.0\ 10^3\ mol^{-2}\ L^{-2}\ min^{-1}$; (d) 0.0050 mol/L; (e) Step II is the rate-determining step. If step I gives N_2O_2 in adequate amount, steps 1 and 2 combine to give This reaction corresponds to the observed rate law. Combine steps 1 and 2 with step 3, which occurs by supposition in a rapid fashion, to give the appropriate stoichiometry.

76.

The general mode of action for a catalyst is to provide a mechanism by which the reactants can unite more readily by taking a path with a lower reaction energy. The rates of both the forward and the reverse reactions are increased, leading to a faster achievement of equilibrium.

78.

(a) Chlorine atoms are a catalyst because they react in the second step but are regenerated in the third step. Thus, they are not used up, which is a characteristic of catalysts. (b) NO is a catalyst for the same reason as in part (a).

80.

The lowering of the transition state energy indicates the effect of a catalyst. (a) B; (b) B

82.

The energy needed to go from the initial state to the transition state is (a) 10 kJ; (b) 10 kJ.

84.

Both diagrams describe two-step, exothermic reactions, but with different changes in enthalpy, suggesting the diagrams depict two different overall reactions.

10.14.8: Chapter 8 - Kinetics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 12** is licensed CC BY 4.0.

10.14.9: Chapter 9 - Electrochemistry

1.

(a) reduction; (b) oxidation; (c) oxidation; (d) reduction

3.

(a) (b) (c) (d)

5.

Oxidized: (a) Sn^{2+}; (b) Hg; (c) Al; reduced: (a) H_2O_2; (b) PbO_2; (c) oxidizing agent: (a) H_2O_2; (b) PbO_2; (c) reducing agent: (a) Sn^{2+}; (b) Hg; (c) Al

7.

Oxidized = reducing agent: (a) (b) $Mn(OH)_2$; (c) H_2; (d) Al; reduced = oxidizing agent: (a) $Cu(OH)_2$; (b) O_2; (c) (d)

9.

In basic solution, $[OH^-] > 1\ 10^{-7}\ M > [H^+]$. Hydrogen ion cannot appear as a reactant because its concentration is essentially zero. If it were produced, it would instantly react with the excess hydroxide ion to produce water. Thus, hydrogen ion should *not* appear as a reactant or product in basic solution.

11.

(a) (b) (c) (d)

13.

(a) (b)

15.

Species oxidized = reducing agent: (a) Al(*s*); (b) NO(*g*); (c) Mg(*s*); and (d) MnO_2(*s*); Species reduced = oxidizing agent: (a) Zr^{4+}(*aq*); (b) Ag^+(*aq*); (c) ; and (d)

17.

Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

19.

Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.

21.

(a) +2.115 V (spontaneous); (b) +0.4626 V (spontaneous); (c) +1.0589 V (spontaneous); (d) +0.727 V (spontaneous)

23.

+1.16 V; spontaneous

25.

−1.259 V; nonspontaneous

27.

(a) 0 kJ/mol; (b) −83.7 kJ/mol; (c) +235.3 kJ/mol

29.

(a) standard cell potential: 1.50 V, spontaneous; cell potential under stated conditions: 1.43 V, spontaneous; (b) standard cell potential: 1.405 V, spontaneous; cell potential under stated conditions: 1.423 V, spontaneous; (c) standard cell potential: −2.749 V, nonspontaneous; cell potential under stated conditions: −2.757 V, nonspontaneous

31.

(a) $1.7\ 10^{-10}$; (b) $2.6\ 10^{-21}$; (c) $4.693\ 10^{21}$; (d) $1.0\ 10^{-14}$

33.

(a) (b) $3.5\ 10^{15}$; (c) $5.6\ 10^{-9}\ M$

34.

Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.

36.

E_{cell}, as described in the Nernst equation, has a term that is directly proportional to temperature. At low temperatures, this term is decreased, resulting in a lower cell voltage provided by the battery to the device—the same effect as a battery running dead.

38.

Mg and Zn

40.

Both examples involve cathodic protection. The (sacrificial) anode is the metal that corrodes (oxidizes or reacts). In the case of iron (−0.447 V) and zinc (−0.7618 V), zinc has a more negative standard reduction potential and so serves as the anode. In the case of iron and copper (0.34 V), iron has the smaller standard reduction potential and so corrodes (serves as the anode).

42.

While the reduction potential of lithium would make it capable of protecting the other metals, this high potential is also indicative of how reactive lithium is; it would have a spontaneous reaction with most substances. This means that the lithium would react quickly with other substances, even those that would not oxidize the metal it is attempting to protect. Reactivity like this means the sacrificial anode would be depleted rapidly and need to be replaced frequently. (Optional additional reason: fire hazard in the presence of water.)

46.

(a) (b) (c) (d)

48.

0.79 L

10.14.9: Chapter 9 - Electrochemistry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Chapter 17** is licensed CC BY 4.0.

Index

D

delocalization
3.6: Resonance

R

resonance contributors
3.7: Rules for Resonance Forms

resonance forms
3.6: Resonance

resonance hybride
3.7: Rules for Resonance Forms

T

titrations
7.8: Acid-Base Titrations

Glossary

Accuracy | how closely a measurement aligns with a correct value

Acid anhydride | compound that reacts with water to form an acid or acidic solution

Acid ionization | reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

Acid ionization constant (K_a) | equilibrium constant for the ionization of a weak acid

Acid-base indicator | organic acid or base whose color changes depending on the pH of the solution it is in

Acidic | describes a solution in which $[H_3O^+] > [OH^-]$

Actinide | inner transition metal in the bottom of the bottom two rows of the periodic table

Actinide series | (also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

Activated complex | (also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

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

Active electrode | electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

Actual yield | amount of product formed in a reaction

Addition reaction | reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

Adhesive force | force of attraction between molecules of different chemical identities

Alcohol | organic compound with a hydroxyl group (–OH) bonded to a carbon atom

Alkali metal | element in group 1

Alkaline earth metal | element in group 2

Alkaline earth metal | any of the metals (beryllium, magnesium, calcium, strontium, barium, and radium) occupying group 2 of the periodic table; they are reactive, divalent metals that form basic oxides

Alkane | molecule consisting of only carbon and hydrogen atoms connected by single (σ) bonds

Alkene | molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

Alkyl group | substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

Alkyne | molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

Allotropes | two or more forms of the same element, in the same physical state, with different chemical structures

Alloy | solid mixture of a metallic element and one or more additional elements

Alpha (α) decay | loss of an alpha particle during radioactive decay

Alpha particle | (α or $^4_2\mathrm{He}$ or $^4_2\alpha$) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

Alpha particle (α particle) | positively charged particle consisting of two protons and two neutrons

Amide | organic molecule that features a nitrogen atom connected to the carbon atom in a carbonyl group

Amine | organic molecule in which a nitrogen atom is bonded to one or more alkyl group

Amorphous | solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

Amorphous solid | (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

Amphiphilic | molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

Amphiprotic | species that may either gain or lose a proton in a reaction

Amphoteric | species that can act as either an acid or a base

Amplitude | extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

Analyte | chemical species of interest

Angular momentum quantum number (l) | quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

Anion | negatively charged atom or molecule (contains more electrons than protons)

Anode | electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

Antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

Aqueous solution | solution for which water is the solvent

Aromatic hydrocarbon | cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

Arrhenius equation | mathematical relationship between the rate constant and the activation energy of a reaction

Atmosphere (atm) | unit of pressure; 1 atm = 101,325 Pa

Atom | smallest particle of an element that can enter into a chemical combination

Atomic mass | average mass of atoms of an element, expressed in amu

Atomic mass unit (amu) | (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a $^{12}\mathrm{C}$ atom

Atomic number (Z) | number of protons in the nucleus of an atom

Atomic orbital | mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

Aufbau principle | procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

Autoionization | reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

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

Avogadro's number (N_A) | experimentally determined value of the number of entities comprising 1 mole of substance, equal to $6.022 \times 10^{23}\ \mathrm{mol}^{-1}$

Axial position | location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

Balanced equation | chemical equation with equal numbers of atoms for each element in the reactant and product

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

Bar | (bar or b) unit of pressure; 1 bar = 100,000 Pa

Barometer | device used to measure atmospheric pressure

Base anhydride | metal oxide that behaves as a base towards acids

Base ionization | reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Base ionization constant (K_b) | equilibrium constant for the ionization of a weak base

Basic | describes a solution in which $[H_3O^+] < [OH^-]$

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 | (β or $^0_{-1}\mathrm{e}$ or $^0_{-1}\beta$) high-energy electron

Bicarbonate anion | salt of the hydrogen carbonate ion, HCO_3^-

Bidentate ligand | ligand that coordinates to one central metal through coordinate bonds from two different atoms

Binary acid | compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Binary compound | compound containing two different elements.

Binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

Bismuth | heaviest member of group 15; a less reactive metal than other representative metals

Blackbody | idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

Body-centered cubic (BCC) solid | crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

Body-centered cubic unit cell | simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bohr's model of the hydrogen atom | structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

Boiling point | temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Boiling point elevation | elevation of the boiling point of a liquid by addition of a solute

Boiling point elevation constant | the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

Bomb calorimeter | device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

Bond angle | angle between any two covalent bonds that share a common atom

Bond dipole moment | separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

Bond distance | (also, bond length) distance between the nuclei of two bonded atoms

Bond energy | (also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Bond length | distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

Borate | compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

Born-Haber cycle | thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

Bragg equation | equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

Brønsted-Lowry acid | proton donor

Brønsted-Lowry base | proton acceptor

Buffer | mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Buffer capacity | amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

Buret | device used for the precise delivery of variable liquid volumes, such as in a titration analysis

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

Capillary action | flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

Carbonate | salt of the anion CO_3^{2-}; often formed by the reaction of carbon dioxide with bases

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

Cathode | electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

Cathodic protection | method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

Cation | positively charged atom or molecule (contains fewer electrons than protons)

Cell notation | shorthand way to represent the reactions in an electrochemical cell

Cell potential | difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

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

Central metal | ion or atom to which one or more ligands is attached through coordinate covalent bonds

Chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

Chalcogen | element in group 16

Chelate | complex formed from a polydentate ligand attached to a central metal

Chelating ligand | ligand that attaches to a central metal ion by bonds from two or more donor atoms

Chemical change | change producing a different kind of matter from the original kind of matter

Chemical equation | symbolic representation of a chemical reaction

Chemical property | behavior that is related to the change of one kind of matter into another kind of matter

Chemical reduction | method of preparing a representative metal using a reducing agent

Chemical symbol | one-, two-, or three-letter abbreviation used to represent an element or its atoms

Chemical thermodynamics | area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

Chemistry | study of the composition, properties, and interactions of matter

Chemotherapy | similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

Chlor-alkali process | electrolysis process for the synthesis of chlorine and sodium hydroxide

Circuit | path taken by a current as it flows because of an electrical potential difference

***cis* configuration** | configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

Clausius-Clapeyron equation | mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

Coefficient | number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

Cohesive force | force of attraction between identical molecules

Colligative property | property of a solution that depends only on the concentration of a solute species

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

Colloid | (also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

Color-change interval | range in pH over which the color change of an indicator takes place

Combustion analysis | gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

Common ion effect | effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

Complete ionic equation | chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

Compound | pure substance that can be decomposed into two or more elements

Compressibility factor (Z) | ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

Concentrated | qualitative term for a solution containing solute at a relatively high concentration

Concentration | quantitative measure of the relative amounts of solute and solvent present in a solution

Concentration cell | galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

Condensation | change from a gaseous to a liquid state

Conjugate acid | substance formed when a base gains a proton

Conjugate base | substance formed when an acid loses a proton

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

Continuous spectrum | electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

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

Coordination compound | stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

Coordination compound | substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

Coordination number | number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

Coordination number | number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

Coordination sphere | central metal atom or ion plus the attached ligands of a complex

Core electron | electron in an atom that occupies the orbitals of the inner shells

Corrosion | degradation of metal through an electrochemical process

Covalent bond | attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

Covalent bond | bond formed when electrons are shared between atoms

Covalent compound | (also, molecular compound) composed of molecules formed by atoms of two or more different elements

Covalent network solid | solid whose particles are held together by covalent bonds

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

Crenation | process whereby biological cells become shriveled due to loss of water by osmosis

Critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

Critical point | temperature and pressure above which a gas cannot be condensed into a liquid

Crystal field splitting (Δ_{oct}) | difference in energy between the t_{2g} and e_g sets or t and e sets of orbitals

Crystal field theory | model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

Crystalline solid | solid in which the particles are arranged in a definite repeating pattern

Cubic centimeter (cm^3 or cc) | volume of a cube with an edge length of exactly 1 cm

Cubic closest packing (CCP) | crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

Cubic meter (m^3) | SI unit of volume

Curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Current | flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(1\ \text{A} = 1\ \frac{\text{C}}{\text{s}}\right)$

***d* orbital** | region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a *d* electron

***d*-block element** | one of the elements in groups 3–11 with valence electrons in *d* orbitals

Dalton (Da) | alternative unit equivalent to the atomic mass unit

Dalton's atomic theory | set of postulates that established the fundamental properties of atoms

Daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

Density | ratio of mass to volume for a substance or object

Deposition | change from a gaseous state directly to a solid state

Diffraction | redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

Dilute | qualitative term for a solution containing solute at a relatively low concentration

Dilution | process of adding solvent to a solution in order to lower the concentration of solutes

Dimensional analysis | (also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Dipole moment | property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

Dipole-dipole attraction | intermolecular attraction between two permanent dipoles

Diprotic acid | acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

Diprotic base | base capable of accepting two protons. The protons are accepted in two steps

Dispersed phase | substance present as relatively large solid or liquid particles in a colloid

Dispersion force | (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

Dispersion medium | solid, liquid, or gas in which colloidal particles are dispersed

Disproportionation reaction | chemical reaction where a single reactant is simultaneously reduced and oxidized; it is both the reducing agent and the oxidizing agent

Dissociation | physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

Dissolved | describes the process by which solute components are dispersed in a solvent

Donor atom | atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

Double bond | covalent bond in which two pairs of electrons are shared between two atoms

Downs cell | electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

Dynamic equilibrium | state of a system in which reciprocal processes are occurring at equal rates

Effective nuclear charge | charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

***e_g* orbitals** | set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

Electrical potential | energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1\ \text{V} = 1\ \frac{\text{J}}{\text{C}}\right)$

Electrical work (w_{ele}) | negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Electrolyte | substance that produces ions when dissolved in water

Electromagnetic radiation | energy transmitted by waves that have an electric-field component and a magnetic-field component

Electromagnetic spectrum | range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

Electron | negatively charged, subatomic particle of relatively low mass located outside the nucleus

Electron affinity | energy required to add an electron to a gaseous atom to form an anion

Electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

Electron configuration | electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Electron density | a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

Electron 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

Electron-pair geometry | arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

Electronegativity | tendency of an atom to attract electrons in a bond to itself

Element | substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

Empirical formula | formula showing the composition of a compound given as the simplest whole-number ratio of atoms

Empirical formula mass | sum of average atomic masses for all atoms represented in an empirical formula

Emulsifying agent | amphiphilic substance used to stabilize the particles of some emulsions

Emulsion | colloid formed from immiscible liquids

End point | measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

Endothermic process | chemical reaction or physical change that absorbs heat

Energy | capacity to supply heat or do work

Enthalpy (*H*) | sum of a system's internal energy and the mathematical product of its pressure and volume

Enthalpy change (ΔH) | heat released or absorbed by a system under constant pressure during a chemical or physical process

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

Equatorial position | one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

Equilibrium | in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

Equilibrium constant (*K*) | value of the reaction quotient for a system at equilibrium

Equivalence point | volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

Ether | organic compound with an oxygen atom that is bonded to two carbon atoms

Exact number | number derived by counting or by definition

Excess reactant | reactant present in an amount greater than required by the reaction stoichiometry

Excited state | state having an energy greater than the ground-state energy

Exothermic process | chemical reaction or physical change that releases heat

Expansion work (pressure-volume work) | work done as a system expands or contracts against external pressure

Extensive property | property of a substance that depends on the amount of the substance

External beam radiation therapy | radiation delivered by a machine outside the body

***f* orbital** | multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an *f* electron

***f*-block element** | (also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

Face-centered cubic (FCC) solid | crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

Face-centered cubic unit cell | simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

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

Faraday's constant (F) | charge on 1 mol of electrons; $F = 96{,}485$ C/mol e^-

First law of thermodynamics | internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

First transition series | transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

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

Formal charge | charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

Formula mass | sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

Fourth transition series | transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

Frasch process | important in the mining of free sulfur from enormous underground deposits

Free radical | molecule that contains an odd number of electrons

Freezing | change from a liquid state to a solid state

Freezing point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

Freezing point depression | lowering of the freezing point of a liquid by addition of a solute

Freezing point depression constant | (also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

Frequency (ν) | number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

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

Functional group | part of an organic molecule that imparts a specific chemical reactivity to the molecule

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

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

Galvanic cell | electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

Galvanized iron | method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

Gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

Gamma ray | (γ or ${}^{0}_{0}\gamma$) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Gas | state in which matter has neither definite volume nor shape

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

Gel | colloidal dispersion of a liquid in a solid

Geometric isomers | isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

Gibbs free energy change (*G*) | thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

Gravimetric analysis | quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

Gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

Ground state | state in which the electrons in an atom, ion, or molecule have the lowest energy possible

Group | vertical column of the periodic table

Haber process | main industrial process used to produce ammonia from nitrogen and hydrogen; involves the use of an iron catalyst and elevated temperatures and pressures

Half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

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

Half-reaction method | method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation "half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

Halide | compound containing an anion of a group 17 element in the 1− oxidation state (fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-)

Hall–Héroult cell | electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

Halogen | element in group 17

Heat (*q*) | transfer of thermal energy between two bodies

Heat capacity (*C*) | extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

Heisenberg uncertainty principle | rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

Hemolysis | rupture of red blood cells due to the accumulation of excess water by osmosis

Henderson-Hasselbalch equation | equation used to calculate the pH of buffer solutions

Henry's law | law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

Hertz (Hz) | the unit of frequency, which is the number of cycles per second, s^{-1}

Hess's law | if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

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

Heterogeneous equilibria | equilibria between reactants and products in different phases

Heterogeneous mixture | combination of substances with a composition that varies from point to point

Hexagonal closest packing (HCP) | crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

High-spin complex | complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

Hole | (also, interstice) space between atoms within a crystal

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

Homogeneous equilibria | equilibria within a single phase

Homogeneous mixture | (also, solution) combination of substances with a composition that is uniform throughout

Hund's rule | every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

Hydrocarbon | compound composed only of hydrogen and carbon; the major component of fossil fuels

Hydrogen bonding | occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

Hydrogen carbonate | salt of carbonic acid, H_2CO_3 (containing the anion HCO_3^-) in which one hydrogen atom has been replaced; an acid carbonate; also known as *bicarbonate ion*

Hydrogen halide | binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

Hydrogen sulfate | HSO_4^- ion

Hydrogen sulfite | HSO_3^- ion

Hydrogenation | addition of hydrogen (H_2) to reduce a compound

Hydrometallurgy | process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

Hydrostatic pressure | pressure exerted by a fluid due to gravity

Hydroxide | compound of a metal with the hydroxide ion OH^- or the group −OH

Hypertonic | of greater osmotic pressure

Hypervalent molecule | molecule containing at least one main group element that has more than eight electrons in its valence shell

Hypothesis | tentative explanation of observations that acts as a guide for gathering and checking information

Hypotonic | of less osmotic pressure

Ideal solution | solution that forms with no accompanying energy change

Immiscible | of negligible mutual solubility; typically refers to liquid substances

Indicator | substance added to the sample in a titration analysis to permit visual detection of the end point

Induced dipole | temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

Inert electrode | electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

Inert gas | (also, noble gas) element in group 18

Inert pair effect | tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

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

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

Instantaneous dipole | temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

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

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

Intensity | property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

Intensive property | property of a substance that is independent of the amount of the substance

Interference pattern | pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

Interhalogen | compound formed from two or more different halogens

Intermolecular force | noncovalent attractive force between atoms, molecules, and/or ions

Internal energy (U) | total of all possible kinds of energy present in a substance or substances

Internal radiation therapy | (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

Interstitial sites | spaces between the regular particle positions in any array of atoms or ions

Ion | electrically charged atom or molecule (contains unequal numbers of protons and electrons)

Ion pair | solvated anion/cation pair held together by moderate electrostatic attraction

Ion-dipole attraction | electrostatic attraction between an ion and a polar molecule

Ion-product constant for water (K_w) | equilibrium constant for the autoionization of water

Ionic bond | electrostatic forces of attraction between the oppositely charged ions of an ionic compound

Ionic bond | strong electrostatic force of attraction between cations and anions in an ionic compound

Ionic compound | compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

Ionic solid | solid composed of positive and negative ions held together by strong electrostatic attractions

Ionization energy | energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

Ionization isomer | (or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

Ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

Isoelectronic | group of ions or atoms that have identical electron configurations

Isomers | compounds with the same chemical formula but different structures

Isomorphous | possessing the same crystalline structure

Isotonic | of equal osmotic pressure

Isotopes | atoms that contain the same number of protons but different numbers of neutrons

Joule (J) | SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

K_c | equilibrium constant for reactions based on concentrations of reactants and products

Kelvin (K) | SI unit of temperature; 273.15 K = 0 ºC

Kilogram (kg) | standard SI unit of mass; 1 kg = approximately 2.2 pounds

Kinetic energy | energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

K_P | equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

Lanthanide | inner transition metal in the top of the bottom two rows of the periodic table

Lanthanide series | (also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

Lattice energy ($\Delta H_{lattice}$) | energy required to separate one mole of an ionic solid into its component gaseous ions

Law | statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

Law of conservation of matter | when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

Law of constant composition | (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

Law of definite proportions | (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

Law of mass action | when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Law of multiple proportions | when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Le Chatelier's principle | when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

Length | measure of one dimension of an object

Leveling effect of water | any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

Lewis structure | diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol | symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

Ligand | ion or neutral molecule attached to the central metal ion in a coordination compound

Limiting reactant | reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

Line spectrum | electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

Linear | shape in which two outside groups are placed on opposite sides of a central atom

Linkage isomer | coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

Liquid | state of matter that has a definite volume but indefinite shape

Liter (L) | (also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

Lone pair | two (a pair of) valence electrons that are not used to form a covalent bond

Low-spin complex | complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

Macroscopic domain | realm of everyday things that are large enough to sense directly by human sight and touch

Magic number | nuclei with specific numbers of nucleons that are within the band of stability

Magnetic quantum number (m_l) | quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

Main-group element | (also, representative element) element in columns 1, 2, and 12–18

Manometer | device used to measure the pressure of a gas trapped in a container

Mass | fundamental property indicating amount of matter

Mass 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 number (A) | sum of the numbers of neutrons and protons in the nucleus of an atom

Mass percentage | ratio of solute-to-solution mass expressed as a percentage

Mass-energy equivalence equation | Albert Einstein's relationship showing that mass and energy are equivalent

Mass-volume percent | ratio of solute mass to solution volume, expressed as a percentage

Matter | anything that occupies space and has mass

Melting | change from a solid state to a liquid state

Melting point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

Metal | element that is shiny, malleable, good conductor of heat and electricity

Metal (representative) | atoms of the metallic elements of groups 1, 2, 12, 13, 14, 15, and 16, which form ionic compounds by losing electrons from their outer *s* or *p* orbitals

Metallic solid | solid composed of metal atoms

Metalloid | element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

Metalloid | element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

Meter (m) | standard metric and SI unit of length; 1 m = approximately 1.094 yards

Method of initial rates | use of a more explicit algebraic method to determine the orders in a rate law

Microscopic domain | realm of things that are much too small to be sensed directly

Microstate (W) | possible configuration or arrangement of matter and energy within a system

Millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Milliliter (mL) | 1/1,000 of a liter; equal to 1 cm^3

Miscible | mutually soluble in all proportions; typically refers to liquid substances

Mixture | matter that can be separated into its components by physical means

Molality (m) | a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

Molar mass | mass in grams of 1 mole of a substance

Molar solubility | solubility of a compound expressed in units of moles per liter (mol/L)

Molarity (M) | unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

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

Molecular compound | (also, covalent compound) composed of molecules formed by atoms of two or more different elements

Molecular equation | chemical equation in which all reactants and products are represented as neutral substances

Molecular formula | formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

Molecular solid | solid composed of neutral molecules held together by intermolecular forces of attraction

Molecular structure | arrangement of atoms in a molecule or ion

Molecular structure | structure that includes only the placement of the atoms in the molecule

Molecule | bonded collection of two or more atoms of the same or different elements

Monatomic ion | ion composed of a single atom

Monodentate | ligand that attaches to a central metal through just one coordinate covalent bond

Monoprotic acid | acid containing one ionizable hydrogen atom per molecule

Multiple equilibrium | system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

Nernst equation | equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

Net ionic equation | chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

Neutral | describes a solution in which $[H_3O^+] = [OH^-]$

Neutron | uncharged, subatomic particle located in the nucleus

Nitrate | NO_3^- ion; salt of nitric acid

Nitrogen fixation | formation of nitrogen compounds from molecular nitrogen

Noble gas | (also, inert gas) element in group 18

Node | any point of a standing wave with zero amplitude

Node | plane separating different lobes of orbitals, where the probability of finding an electron is zero

Nomenclature | system of rules for naming objects of interest

Nonelectrolyte | substance that does not produce ions when dissolved in water

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

Nonmetal | element that appears dull, poor conductor of heat and electricity

Nonspontaneous process | process that requires continual input of energy from an external source

Normal boiling point | temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

Nuclear 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

Nucleus | massive, positively charged center of an atom made up of protons and neutrons

Nuclide | nucleus of a particular isotope

Nutritional calorie (Calorie) | unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

Octahedral | shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

Octahedral hole | open space in a crystal at the center of six particles located at the corners of an octahedron

Octet rule | guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

Optical isomer | (also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

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

Organic compound | natural or synthetic compound that contains carbon

Osmosis | diffusion of solvent molecules through a semipermeable membrane

Osmotic pressure (Π) | opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Ostwald process | industrial process used to convert ammonia into nitric acid

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

Overlap | coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

Oxidation half-reaction | the "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

Oxide | binary compound of oxygen with another element or group, typically containing O^{2-} ions or the group –O– or =O

Oxyacid | compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Oxyacid | compound containing a nonmetal and one or more hydroxyl groups

Oxyanion | polyatomic anion composed of a central atom bonded to oxygen atoms

Ozone | allotrope of oxygen; O_3

***p* orbital** | dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a *p* electron

Pairing energy (P) | energy required to place two electrons with opposite spins into a single orbital

Parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

Partially miscible | of moderate mutual solubility; typically refers to liquid substances

Particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

Parts per billion (ppb) | ratio of solute-to-solution mass multiplied by 10^9

Parts per million (ppm) | ratio of solute-to-solution mass multiplied by 10^6

Pascal (Pa) | SI unit of pressure; 1 Pa = 1 N/m^2

Passivation | metals with a protective nonreactive film of oxide or other compound that creates a barrier for chemical reactions; physical or chemical removal of the passivating film allows the metals to demonstrate their expected chemical reactivity

Pauli exclusion principle | specifies that no two electrons in an atom can have the same value for all four quantum numbers

Percent composition | percentage by mass of the various elements in a compound

Percent ionization | ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Percent yield | measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

Period | (also, series) horizontal row of the periodic table

Periodic law | properties of the elements are periodic function of their atomic numbers.

Periodic table | table of the elements that places elements with similar chemical properties close together

Peroxide | molecule containing two oxygen atoms bonded together or as the anion, O_2^{2-}

PH | logarithmic measure of the concentration of hydronium ions in a solution

Phase diagram | pressure-temperature graph summarizing conditions under which the phases of a substance can exist

Photon | smallest possible packet of electromagnetic radiation, a particle of light

Photosynthesis | process whereby light energy promotes the reaction of water and carbon dioxide to form carbohydrates and oxygen; this allows photosynthetic organisms to store energy

Physical change | change in the state or properties of matter that does not involve a change in its chemical composition

Physical property | characteristic of matter that is not associated with any change in its chemical composition

Pi bond (π bond) | covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

Pidgeon process | chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

Plasma | gaseous state of matter containing a large number of electrically charged atoms and/or molecules

Platinum metals | group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

Pnictogen | element in group 15

POH | logarithmic measure of the concentration of hydroxide ions in a solution

Polar covalent bond | covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

Polar molecule | (also, dipole) molecule with an overall dipole moment

Polarizability | measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

Polyatomic ion | ion composed of more than one atom

Polydentate ligand | ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

Polymorph | variation in crystalline structure that results in different physical properties for the resulting compound

Position of equilibrium | concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

Positron ($_{+1}^{0}\beta$ or $_{+1}^{0}e$) | 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

Potential energy | energy of a particle or system of particles derived from relative position, composition, or condition

Pounds per square inch (psi) | unit of pressure common in the US

Precision | how closely a measurement matches the same measurement when repeated

Pressure | force exerted per unit area

Principal quantum number (*n*) | quantum number specifying the shell an electron occupies in an atom

Product | substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

Proton | positively charged, subatomic particle located in the nucleus

Pure covalent bond | (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

Pure substance | homogeneous substance that has a constant composition

Quantitative analysis | the determination of the amount or concentration of a substance in a sample

Quantization | occurring only in specific discrete values, not continuous

Quantum mechanics | field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

Quantum number | integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

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 $^{14}_{6}C : ^{12}_{6}C$ in the object vs. the ratio of $^{14}_{6}C : ^{12}_{6}C$ 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

Raoult's law | the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

Rare earth element | collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

Rate constant (*k*) | proportionality constant in the relationship between reaction rate and concentrations of reactants

Rate expression | mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

Rate law | (also, rate equation) 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

Reactant | substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

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

Reaction quotient (*Q*) | ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

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

Reduction half-reaction | the "half" of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

Relative biological effectiveness (RBE) | measure of the relative damage done by radiation

Representative element | (also, main-group element) element in columns 1, 2, and 12–18

Representative element | element where the *s* and *p* orbitals are filling

Representative metal | metal among the representative elements

Resonance | situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

Resonance forms | two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

Resonance hybrid | average of the resonance forms shown by the individual Lewis structures

Reversible 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 removed

Reversible reaction | chemical reaction that can proceed in both the forward and reverse directions under given conditions

Roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv

Rounding | procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

***s* orbital** | spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an *s* electron

Sacrificial anode | more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

Saturated | of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

Saturated hydrocarbon | molecule containing carbon and hydrogen that has only single bonds between carbon atoms

Scientific method | path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

Scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

Second (s) | SI unit of time

Second law of thermodynamics | entropy of the universe increases for a spontaneous process

Second transition series | transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

Selective precipitation | process in which ions are separated using differences in their solubility with a given precipitating reagent

Semipermeable membrane | a membrane that selectively permits passage of certain ions or molecules

Series | (also, period) horizontal row of the period table

Shell | set of orbitals with the same principal quantum number, *n*

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

Sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

Sigma bond (σ bond) | covalent bond formed by overlap of atomic orbitals along the internuclear axis

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

Silicate | compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

Simple cubic structure | crystalline structure with a cubic unit cell with lattice points only at the corners

Simple cubic unit cell | (also, primitive cubic unit cell) unit cell in the simple cubic structure

Single bond | bond in which a single pair of electrons is shared between two atoms

Skeletal structure | shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

Smelting | process of extracting a pure metal from a molten ore

Solid | state of matter that is rigid, has a definite shape, and has a fairly constant volume

Solubility | extent to which a solute may be dissolved in water, or any solvent

Solubility product (K_{sp}) | equilibrium constant for the dissolution of a slightly soluble electrolyte

Solute | solution component present in a concentration less than that of the solvent

Solvation | exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

Solvent | solution component present in a concentration that is higher relative to other components

Space lattice | all points within a crystal that have identical environments

Spatial isomers | compounds in which the relative orientations of the atoms in space differ

Specific heat capacity (*c*) | intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

Spectator ion | ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Spectrochemical series | ranking of ligands according to the magnitude of the crystal field splitting they induce

Spin quantum number (m_s) | number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

Spontaneous change | process that takes place without a continuous input of energy from an external source

Spontaneous process | physical or chemical change that occurs without the addition of energy from an external source

Standard cell potential (E°_{cell}) | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

Standard enthalpy of combustion (ΔH_c°) | heat released when one mole of a compound undergoes complete combustion under standard conditions

Standard enthalpy of formation (ΔH_f°) | enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

Standard entropy ($S°$) | entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S°_{298}

Standard entropy change ($\Delta S°$) | change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS°_{298}

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 (ΔG_f°) | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

Standard hydrogen electrode (SHE) | the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

Standard reduction potential ($E°$) | the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

Standard state | set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Standing wave | (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

State function | property depending only on the state of a system, and not the path taken to reach that state

Steel | material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

Stepwise ionization | process in which an acid is ionized by losing protons sequentially

Stress | change to a reaction's conditions that may cause a shift in the equilibrium

Strong electrolyte | substance that dissociates or ionizes completely when dissolved in water

Strong nuclear force | force of attraction between nucleons that holds a nucleus together

Strong-field ligand | ligand that causes larger crystal field splittings

Structural formula | shows the atoms in a molecule and how they are connected

Structural isomer | one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

Subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

Sublimation | change from solid state directly to gaseous state

Subshell | set of orbitals in an atom with the same values of *n* and *l*

Substituent | branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

Substitution reaction | reaction in which one atom replaces another in a molecule

Sulfate | SO_4^{2-} ion

Sulfite | SO_3^{2-} ion

Superconductor | material that conducts electricity with no resistance

Supercritical fluid | substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

Supercritical mass | amount of material in which there is an increasing rate of fission

Superoxide | oxide containing the anion O_2^-

Supersaturated | of concentration that exceeds solubility; a nonequilibrium state

Surface tension | energy required to increase the area, or length, of a liquid surface by a given amount

Surroundings | all matter other than the system being studied

Symbolic domain | specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

System | portion of matter undergoing a chemical or physical change being studied

***t_{2g}* orbitals** | set of three *d* orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

Temperature | intensive property of matter that is a quantitative measure of "hotness" and "coldness"

Tetrahedral | shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

Tetrahedral hole | tetrahedral space formed by four atoms or ions in a crystal

Theoretical yield | amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Theory | well-substantiated, comprehensive, testable explanation of a particular aspect of nature

Thermal energy | kinetic energy associated with the random motion of atoms and molecules

Thermochemistry | study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

Third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

Third transition series | transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

Titrant | solution containing a known concentration of substance that will react with the analyte in a titration analysis

Titration analysis | quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

Titration curve | plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

Torr | unit of pressure; $1\ \text{torr} = \frac{1}{760}\ \text{atm}$

***trans* configuration** | configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

Transition metal | element in columns 3–11

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

Trigonal bipyramidal | shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

Trigonal planar | shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

Triple bond | bond in which three pairs of electrons are shared between two atoms

Triple point | temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

Triprotic acid | acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Tyndall effect | scattering of visible light by a colloidal dispersion

Uncertainty | estimate of amount by which measurement differs from true value

Unified atomic mass unit (u) | alternative unit equivalent to the atomic mass unit

Unit | standard of comparison for measurements

Unit cell | smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

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

Unsaturated | of concentration less than solubility

Vacancy | defect that occurs when a position that should contain an atom or ion is vacant

Valence bond theory | description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

Valence electrons | electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

Valence shell | outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level (*s* and *p* subshells) are in the valence shell, while for transition metals, the highest energy *s* and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d*, and *f* subshells are included

Valence shell electron-pair repulsion theory (VSEPR) | theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

Van der Waals equation | modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Van der Waals force | attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Van't Hoff factor (*i*) | the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Vapor pressure | (also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

Vaporization | change from liquid state to gaseous state

Vector | quantity having magnitude and direction

Viscosity | measure of a liquid's resistance to flow

Voltaic cell | another name for a galvanic cell

Volume | amount of space occupied by an object

Volume percentage | ratio of solute-to-solution volume expressed as a percentage

Wave | oscillation that can transport energy from one point to another in space

Wave-particle duality | term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Wavefunction (*ψ*) | mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

Wavelength (*λ*) | distance between two consecutive peaks or troughs in a wave

Weak electrolyte | substance that ionizes only partially when dissolved in water

Weak-field ligand | ligand that causes small crystal field splittings

Weight | force that gravity exerts on an object

Work (*w*) | energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

X-ray crystallography | experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal



Detailed Licensing

Overview

Title: CHM 118: Advanced General Chemistry (Strom)

Webpages: 143

All licenses found:

- CC BY 4.0: 64.3% (92 pages)
- Undeclared: 34.3% (49 pages)
- CC BY-SA 4.0: 1.4% (2 pages)

By Page

- CHM 118: Advanced General Chemistry (Strom) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Radioactivity and Nuclear Chemistry - *Undeclared*
    - 1.1: The Discovery of Radioactivity - *Undeclared*
    - 1.2: Types of Radioactivity - *Undeclared*
    - 1.3: The Valley of Stability- Predicting the Type of Radioactivity - *Undeclared*
    - 1.4: Detecting Radioactivity - *Undeclared*
    - 1.5: The Discovery of Fission- The Atomic Bomb and Nuclear Power - *CC BY 4.0*
    - 1.6: Converting Mass to Energy- Mass Defect and Nuclear Binding Energy - *Undeclared*
    - 1.7: Nuclear Fusion - The Power of the Sun - *Undeclared*
    - 1.8: Nuclear Transmutation and Transuranium Elements - *Undeclared*
    - 1.9: The Effects of Radiation on Life - *Undeclared*
    - 1.10: Radioactivity in Medicine and Other Applications - *Undeclared*
    - 1.11: Key Terms - *CC BY 4.0*
    - 1.12: Key Equations - *CC BY 4.0*
    - 1.13: Summary - *CC BY 4.0*
    - 1.14: Exercises - *CC BY 4.0*
  - 2: Chemical Bonding and Molecular Geometry - *CC BY 4.0*
    - 2.1: Introduction - *CC BY 4.0*
    - 2.2: Ionic Bonding - *CC BY 4.0*
    - 2.3: Covalent Bonding - *CC BY 4.0*
    - 2.4: Lewis Symbols and Structures - *CC BY 4.0*
    - 2.5: Introduction to Formal Charges and Resonance - *CC BY 4.0*
    - 2.6: Molecular Structure and Polarity - *CC BY 4.0*
    - 2.7: Key Terms - *Undeclared*
    - 2.8: Key Equations - *Undeclared*
    - 2.9: Summary - *Undeclared*
    - 2.10: Exercises - *CC BY 4.0*
  - 3: Advanced Theories of Covalent Bonding - *CC BY 4.0*
    - 3.1: Introduction - *CC BY 4.0*
    - 3.2: Molecular Orbital Theory - *CC BY 4.0*
    - 3.3: Valence Bond Theory - *CC BY 4.0*
    - 3.4: Hybrid Atomic Orbitals - *CC BY 4.0*
    - 3.5: Multiple Bonds formed between Hybridized Atoms - *CC BY 4.0*
    - 3.6: Resonance - *CC BY-SA 4.0*
    - 3.7: Rules for Resonance Forms - *CC BY-SA 4.0*
    - 3.8: Resonance Effects on Hybridization and Bonding - *CC BY 4.0*
    - 3.9: Hybridized Orbital Energy Diagrams - *Undeclared*
    - 3.10: Key Terms - *Undeclared*
    - 3.11: Summary - *Undeclared*
    - 3.12: Exercises - *CC BY 4.0*
  - 4: Thermochemistry - *CC BY 4.0*
    - 4.1: Introduction - *CC BY 4.0*
    - 4.2: Energy Basics - *CC BY 4.0*
    - 4.3: Calorimetry - *CC BY 4.0*
    - 4.4: Enthalpy - *CC BY 4.0*
    - 4.5: Strengths of Ionic and Covalent Bonds - *Undeclared*
    - 4.6: Key Terms - *Undeclared*
    - 4.7: Key Equations - *Undeclared*
    - 4.8: Summary - *Undeclared*
    - 4.9: Exercises - *CC BY 4.0*
  - 5: Thermodynamics - *CC BY 4.0*
    - 5.1: Introduction - *Undeclared*
    - 5.2: Spontaneity - *CC BY 4.0*
    - 5.3: Entropy - *CC BY 4.0*
    - 5.4: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
    - 5.5: Free Energy - *CC BY 4.0*
    - 5.6: Key Terms - *Undeclared*

- 5.7: Key Equations - *Undeclared*
- 5.8: Summary - *Undeclared*
- 5.9: Exercises - *CC BY 4.0*

- 6: Fundamental Equilibrium Concepts - *CC BY 4.0*
  - 6.1: Introduction - *CC BY 4.0*
  - 6.2: Chemical Equilibria - *CC BY 4.0*
  - 6.3: Equilibrium Constants - *CC BY 4.0*
  - 6.4: Shifting Equilibria - Le Chatelier's Principle - *CC BY 4.0*
  - 6.5: Equilibrium Calculations - *CC BY 4.0*
  - 6.6: Free Energy Equilibria - *Undeclared*
  - 6.7: Key Terms - *Undeclared*
  - 6.8: Key Equations - *Undeclared*
  - 6.9: Summary - *Undeclared*
  - 6.10: Exercises - *CC BY 4.0*
- 7: Acid-Base Equilibria - *CC BY 4.0*
  - 7.1: Introduction - *Undeclared*
  - 7.2: Brønsted-Lowry Acids and Bases - *CC BY 4.0*
  - 7.3: pH and pOH - *CC BY 4.0*
  - 7.4: Relative Strengths of Acids and Bases - *CC BY 4.0*
  - 7.5: Hydrolysis of Salt - *CC BY 4.0*
  - 7.6: Polyprotic Acids - *CC BY 4.0*
  - 7.7: Buffers - *CC BY 4.0*
  - 7.8: Acid-Base Titrations - *CC BY 4.0*
  - 7.9: Key Terms - *Undeclared*
  - 7.10: Key Equations - *Undeclared*
  - 7.11: Summary - *Undeclared*
  - 7.12: Exercises - *CC BY 4.0*
- 8: Kinetics - *CC BY 4.0*
  - 8.1: Introduction - *CC BY 4.0*
  - 8.2: Chemical Reaction Rates - *CC BY 4.0*
  - 8.3: Factors Affecting Reaction Rates - *CC BY 4.0*
  - 8.4: Rate Laws - *CC BY 4.0*
  - 8.5: Integrated Rate Laws - *CC BY 4.0*
  - 8.6: Collision Theory - *CC BY 4.0*
  - 8.7: Reaction Mechanisms - *CC BY 4.0*
  - 8.8: Catalysis - *CC BY 4.0*
  - 8.9: Key Terms - *Undeclared*
  - 8.10: Key Equations - *Undeclared*
  - 8.11: Summary - *Undeclared*
  - 8.12: Exercises - *CC BY 4.0*
- 9: Electrochemistry - *CC BY 4.0*
  - 9.1: Introduction - *Undeclared*
  - 9.2: Review of Redox Chemistry - *CC BY 4.0*
  - 9.3: Galvanic Cells - *CC BY 4.0*
  - 9.4: Electrode and Cell Potentials - *CC BY 4.0*
  - 9.5: Potential, Free Energy, and Equilibrium - *CC BY 4.0*
  - 9.6: Batteries and Fuel Cells - *CC BY 4.0*
  - 9.7: Corrosion - *CC BY 4.0*
  - 9.8: Electrolysis - *CC BY 4.0*
  - 9.9: Key Terms - *Undeclared*
  - 9.10: Key Equations - *Undeclared*
  - 9.11: Summary - *Undeclared*
  - 9.12: Exercises - *CC BY 4.0*
- 10: Appendices - *CC BY 4.0*
  - 10.1: Appendix A- The Periodic Table - *CC BY 4.0*
  - 10.2: Appendix B- Essential Mathematics - *CC BY 4.0*
  - 10.3: Appendix C- Units and Conversion Factors - *CC BY 4.0*
  - 10.4: Appendix D- Fundamental Physical Constants - *CC BY 4.0*
  - 10.5: Appendix E- Water Properties - *CC BY 4.0*
  - 10.6: Appendix F- Composition of Commercial Acids and Bases - *CC BY 4.0*
  - 10.7: Appendix G- Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
  - 10.8: Appendix H- Ionization Constants of Weak Acids - *CC BY 4.0*
  - 10.9: Appendix I- Ionization Constants of Weak Bases - *CC BY 4.0*
  - 10.10: Appendix J- Solubility Products - *CC BY 4.0*
  - 10.11: Appendix K- Formation Constants for Complex Ions - *CC BY 4.0*
  - 10.12: Appendix L- Standard Electrode (Half-Cell) Potentials - *CC BY 4.0*
  - 10.13: Appendix M- Half-Lives for Several Radioactive Isotopes - *CC BY 4.0*
  - 10.14: Answer Keys - *CC BY 4.0*
    - 10.14.1: Chapter 1 - Radioactivity and Nuclear Chemistry - *CC BY 4.0*
    - 10.14.2: Chapter 2 - Chemical Bonding and Molecular Geometry - *CC BY 4.0*
    - 10.14.3: Chapter 3 - Advanced Theories of Covalent Bonding - *CC BY 4.0*
    - 10.14.4: Chapter 4 - Thermochemistry - *CC BY 4.0*
    - 10.14.5: Chapter 5 - Thermodynamics - *CC BY 4.0*
    - 10.14.6: Chapter 6 - Fundamental Equilibrium Concepts - *CC BY 4.0*
    - 10.14.7: Chapter 7 - Acid-Base Equilibria - *CC BY 4.0*
    - 10.14.8: Chapter 8 - Kinetics - *CC BY 4.0*
    - 10.14.9: Chapter 9 - Electrochemistry - *CC BY 4.0*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*